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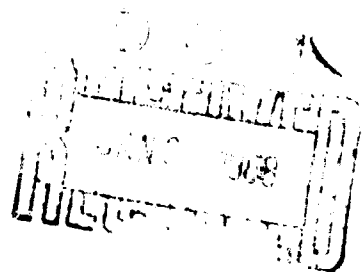
Air Force Office of Scientific Research

Semi Conducting Properties of Cuprous Oxide and Related Research

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Introduction

This report summarizes work carried out under grant number AF-AFOSR-719-65.
Most of the effort was devoted to obtaining a better understanding of the be-
havior of cuprous oxide at high temperatures with special reference to the
electrical properties and defect structure. In this work we were lead to an
investigation of other transition metal oxides. This phase of the work is being
continued under grant number AFOSR-68-1371 so that in some respects this docu-
ment will be in the nature of a progress report. This is true also because a
considerable amount of the early effort was devoted to construction of apparatus
that will be used in subsequent work under the new grant.

In subsequent sections we summarize the main achievements of the work.
Included as an appendix are

(a) Diffusion in Oxides and Sulfides presented at the International
Symposium on Sintering and Related Phenomena at Notre Dame University. As the
publication of the proceedings of this symposium has been delayed the manu-
script is included here for wider circulation.

(b) Preprints of two papers just completed and to be published as part of
the Proceedings of the Symposium on Transport in Oxides held at N.B.S. this
month (October 1967).

Studies on Cuprous Oxide

The major effort here involved construction of an A.C. Hall effect apparatus
for measurements on low mobility materials at high temperatures. The main re-
sults of measurements on pure crystals have been published - "High Temperature
Hall Effect in Cuprous Oxide" by H. L. McKinzie and M. O'Keeffe and will not
be discussed further here.

Two types of thermogravimetric measurement have been made with cuprous
oxide. In the first the kinetics of vaporization were studied in various

atmospherec. The results of this work were presented at the International Symposium on Kinetics of Ionic Reactions at Alfred, N.Y. and will appear in the published proceedings.

Attempts were also made to study the kinetics of change of stoichiometry of the oxide following a rapid change of composition of the surrounding atmosphere. The rapid rate of weight loss by evaporation precluded meaningful measurements so an electrical method was developed for making these studies. The results of this work are included in this report as an appendix.

Studies with other Oxides

The interdiffusion studies by thermogravimetric means have been extended to wüstite (FeO_x). Here there is considerable interest in the effect of defect interactions in this very non-stoichiometric compound. Again a preliminary account of this work is included with this report.

Finally an extensive set of measurements have been made on the thermoelectric power and conductivity of manganous oxide (MnO). To a certain extent these measurements have been overlapped by the work of Hed and Tannhauser [J. Chem. Phys. 47, 2090 (1967)]. However there are still some puzzling problems in the interpretation of these results and their analysis is not yet complete. It is hoped that experiments now underway with doped crystals will shed more light on this problem.

DIFFUSION IN OXIDES AND SULFIDES

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Over the last ten or fifteen years a large body of experimental data has been accumulating on diffusion in oxides and, to a lesser extent, in sulfides. In this review these data are collected together, and an attempt is made to indicate the more interesting of recent developments.

In contrast to, say, the alkali halides, the oxides present an enormous variety of materials with very different properties so that it is difficult to treat the subject in general terms. Because of this diversity of behavior too, there has been little tendency to study any one system in depth, so that despite the number of systems that have been studied, it is probably true that in no instance is our knowledge of the nature and mobility of defects as complete as it is for example in KCl or AgCl.

In an attempt to systematize the discussion, it is convenient at the outset to divide oxides and sulfides into three broad types as follows:

A. Materials with a very small concentration of native defects. 'Very small' may be taken to mean less than that detectable by conventional chemical means (say $< .01\%$). Under this classification will come the oxides and (to a lesser extent) the sulfides of the metals of the first three groups of the periodic table. Li_2O, MgO, Al_2O_3, MgS, etc.

B. Materials in which the defect concentration is more readily measurable, but in which the defects may be considered to be in dilute solution (say .01 to 1%). These materials will be largely transition metal compounds in which more than one cation valency is possible. Examples are: CoO, NiO, Cu_2O.

C. Materials with a large ($> 1\%$) concentration of defects. Well known examples are TiO, FeO, FeS.

The distinction between types B and C has recently been elaborated on by Anderson.[1] It is to be understood that the classification above is

very rough and ready and that a given material may well fall into different types according to conditions of temperature and ambient atmosphere.

We will now discuss diffusion problems that are peculiar to each type separately.

Type A

Materials falling under this heading will have a very low concentration of native defects, which may therefore be expected to show nearly ideal behavior, and there is little doubt that diffusion in a monocrystal will occur by a defect mechanism.

However, for this type of oxide there is a large experimental obstacle to the understanding of the defect structure and hence of diffusion mechanisms. This is, of course, the problem of obtaining crystals of sufficient purity that intrinsic properties of the crystal can be studied. For materials of this type the energy of formation of a defect is very large. If we accept 2ev as a plausible value for the energy of formation of a defect,[2] then the impurity concentration, c, expressed as a fraction of total sites will be

$$c \sim \exp\ (-2ev/kT) \sim 10^{-8} \text{ at } 1000°C$$

It will require only a very small concentration of impurities (e.g. Fe^{3+} in MgO or Al^{3+} in TiO_2) to produce defect concentrations greatly in excess of this intrinsic concentration in the pure crystal. It is very likely, then, that defect controlled properties such as self diffusion will be determined by the fortuitous defect concentration. This is made clear by the work of Wertz and his collaborators who have made an extensive study of defects in MgO and concluded in 1962[3] 'To our knowledge, no MgO crystals have ever been grown which did not show an ESR absorption by one

or more impurity ions. In the best specimen we have observed thus far, iron was present to the extent of 3 parts per million. It is likely, therefore, that many of the electronic properties of magnesium oxide measured to date are to a serious degree affected by the presence of impurities. In addition to direct effects of the ions themselves, one has indirect effects arising from positive-ion vacancies ascribable to the presence of trivalent ions.'

In the same vein, attention is drawn to the work of Kanzaki and co-workers[4] who notice significant effects of impurities on ionic conductivity of KCl with divalent impurity concentrations as low as 0.01 p.p.m.

Despite these rather pessimistic remarks, it is worth enquiring in general terms what type of behavior is expected of oxides of different structural types. Let us consider for example some simple oxides of general formula M_2O, MO and MO_2 and enquire as to whether anion or cation mobility will be the greater.

If the crystals are considered to be an array of charged ions, it is fairly clear that a very important factor in determining the type and mobility of defect in the crystal will be the variation of the electrostatic potential (the Madelung potential) from point to point in the crystal.

The electrostatic potential at an ion site in a simple ionic crystal may readily be evaluated in terms of certain lattice sums[5]. Values that are typical are given for three oxides in Table 1. In the table ϕ_c and ϕ_A are the electrostatic potentials at a cation and anion site respectively arising from the presence of all the other ions in the crystal.

The significance of these potentials is as follows. The work necessary to remove an ion from the otherwise perfect crystal is $-Z\phi$ where Z is the charge on the ion. $Z\phi$ varies roughly as Z^2 (cf Table 1). As a result we

Table 1

Electrostatic potentials at ion sites in oxides

Oxide	Structure	Φ_C (volts)	Φ_A (volts)	$-Z_C\Phi_C$ (eV)	$-Z_A\Phi_A$ (eV)
Na_2O	anti-fluorite	-10.6	19.2	10.6	38.4
MgO	rock salt	-23.9	23.9	47.8	47.8
ZrO_2	fluorite	-43.1	23.2	172.4	46.4

might expect that the formation of defects in which cations are absent from their regular sites, will most readily occur when the cation charge is small. Alternatively, if cation and anion vacancies are present in equal numbers (Schottky defects in a stoichiometric cryst.1) one would expect cation mobility to be greatest when the cation charge is small.

In the act..al energetics of the formation and migration of defects in ionic crystals, relaxation (i.e. polarization) of the cryztal around the defect w'll be very important. In general polarization will favor the formation and migration of vacancies of the less polarizable ion[6] (normally this is the cation) so that in MO (and possibly even in M_2O_3) as well as for M_2O, cation diffusion is likely to be more rapid than anion diffusion. Conversely for MO_2 and higher oxides it is expected that anion diffusion will be more rapid.

Extension of this type of argument suggests that the same general rule will also apply to non-stoichiometric crystals.

It should be remarked that, given the problem of obtaining sufficiently pure crystals, a profitable course to pursue with this type of oxide would be to deliberately dope the crystal with altervalent impurities. There appears to have been very little work done along these lines (with the exception of work on certain fluorite-type oxides mentioned below) in contrast to the very extensive work reported on doped alkali halides. It would be very interesting to study, for example, MgO doped with small quantities of Al_2O_3.

For this type of oxide (type A) there is the attractive feature that electronic conductivity is sometimes negligibly small compared with ionic conductivity. It is usually true also (as discussed above) that one ion is considerably more mobile than the other. If this is the case, the

diffusion coefficient D, for the most mobile species is readily obtained from the conductivity σ using the Nernst-Einstein equation[6]

$$D/\sigma = fkT/(Nq^2)$$ (1)

Here N is the number per unit volume of ions of charge q. f is a numerical factor – the correlation factor - introduced to take into account that successive jumps of the defect may not be entirely random. Normally f is close to unity.[7]

It must, of course, be established that the conductivity is ionic. This has been done for remarkably few oxides. Transport numbers can, however, be measured fairly readily from e.m.f. measurements. Consider for example a concentration cell of the type

$$Pt, \; O_2(P_1) \; \left| \; oxide \; \right| \; Pt, \; O_2(P_2)$$
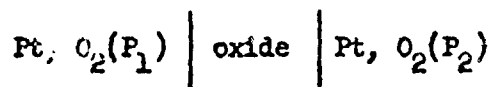
If the oxide were an ionic conductor the e.m.f. of the cell would be given by the familiar Nernst equation:

$$E_{ionic} = (kT/q) \ln (P_1/P_2)^{1/2}$$ (2)

If, on the other hand, there were an appreciably electronic conduction, this would have the effect of partially 'short circuiting' the cell and the e.m.f. would be reduced to [8]

$$E = t_i \; E_{ionic}$$ (3)

where t_i is the ionic transport number. Schmalried[9] has recently given a detailed discussion of this type of measurement and results for several oxides.

As an example of the utility of electrical measurements of this type we may take as an example the results obtained on the mixed oxide $Zr_{1-x}Ca_xO_{2-x}$.

For this oxide the ionic transport number is unity, and the oxygen ions are the most mobile species. D for oxygen has been measured directly by tracer methods (see Table 3) and is in excellent agreement with that calculated from electrical conductivity using equation (1).[10] The importance of transport number measurements is illustrated by results for ThO_2-Y_2O_3 solid solutions which might be expected to behave very similarly to ZrO_2-CaO, but which in fact showed predominantly electronic conductivity.[11] Similar measurements have also been made on pure MgO but with conflicting results.[12]

Type B

For this type of oxide the situation is rather different. Here deviations from stoichiometry are sufficiently large that the native defect concentration is far greater than the normal level of foreign atom concentration in the absence of deliberate doping. In these materials too, the conductivity is almost certainly electronic.

In several instances it has proved possible to measure departures from stoichiometry, either by chemical means (e.g. by analysis for Co^{3+} in CoO_{1+x}[13]) or gravimetrically (e.g. for Cu_2O_{1+x}[14]). If it is assumed that one type of ionic defect predominates in the material, the analysis will give the defect concentration directly. As an example, if the only ionic defect in CoO_{1+x} were cation vacancies (as is thought to be the case), then there are x vacancies per cobalt ion.

In general the diffusion coefficient D is given in terms of the atom fraction c_i of defects responsible for diffusion by

$$D = f\, D_i c_i \qquad (4)$$

Here D_i is the diffusion coefficient for the defect and f is the correlation factor mentioned already. Knowledge of c_i therefore enables D_i to be

calculated from the tracer diffusion coefficient D.

For a dilute solution of defects we can express the temperature and pressure dependence of c_1 in terms of thermodynamic quantities as follows. We take as an example an oxide MO in which cation vacancies and M^{3+} ions are formed in incorporating an excess of oxygen. In terms of Kroger's notation the reaction is

$$\frac{1}{2} O_2 \longrightarrow O_o + V_M' + h^\bullet \tag{5}$$
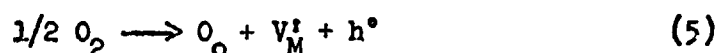
Here O_o is an oxygen ion on an oxygen ion site. V_M is a vacancy made by removing a M _atom_ from a metal ion site. We have assumed that this vacancy is 'ionized', i.e. that it has lost one of the positive charges associated with this site. The positive charge is represented by $h^\bullet$ - it may alternatively be thought of as a M^{3+} ion in the crystal. The equilibrium constant for the reaction (5) is

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \frac{a(h^\bullet)\, a(V_M')\, a(O_o)}{\left[a(O_2)\right]^{1/2}} \tag{6}$$

The activity of O_o is constant and may be chosen to be unity. For a dilute solution, we may replace the activity of defects by concentrations:

$$a(V_M') = a(h^\bullet) = c_1 \tag{7}$$

and

$$a(O_2) = P_{O_2} \tag{8}$$

From (6), (7) and (8) we have immediately

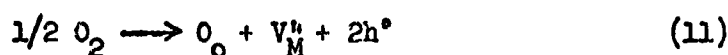$$c_1 = \exp\left(-\Delta G^\circ/2RT\right) P_{O_2}^{1/4} \tag{9}$$

Note that ΔG° is the standard free energy change for reaction (5).

At constant oxygen pressure we have

$$\frac{\partial \ln c_i}{\partial (1/T)} = \frac{-\Delta H^\circ}{2R} \tag{10}$$

ΔH° is now the standard enthalpy change of reaction (5), or stated differently ΔH° is the heat of solution of 1 g. atom of oxygen in MO_{1+x}.

Note that if, instead of reaction (5) we had the vacancy doubly ionized:

$$\tfrac{1}{2} O_2 \longrightarrow O_o + V_M'' + 2h^\bullet \tag{11}$$

then c_i would be given by

$$c_i = (1/4)^{1/3} \exp(-\Delta G^\circ/3RT) P_{O_2}^{1/6} \tag{12}$$

In general

$$c_i \propto \exp(-\Delta G^\circ/nRT)\, P_{O_2}^{1/2n} \tag{13}$$

and

$$\frac{\partial \ln c_i}{\partial(1/T)} = \frac{-\Delta H^\circ}{nR} \tag{14}$$

where, as before, ΔH° is the heat of solution of 1 g. atom of oxygen in the oxide. The value of n can be determined from the oxygen pressure dependence of c_i (equation (13)).

D_i will likewise depend on temperature. A convenient expression for D_i is given by the transition state theory of Eyring.[15]

$$D_i = (kT/h)\, a^2 \exp(\Delta S^{\ddagger}/R)\, \exp(-\Delta H^{\ddagger}/RT) \tag{15}$$

$\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ may be thought of as respectively the entropy and enthalpy of activation for the elementary jump process in diffusion, a is the jump distance and k and h are Boltzmann's and Planck's constants respectively.

From equation (4), (13) and (15) it is clear that if c_i and D are known as functions of temperature, ΔH°, $\Delta H^{\ddagger}$, ΔS° and $\Delta S^{\ddagger}$ may be found.

Data for several oxides have been analyzed by O'Keeffe and Moore[14].
Table 2 lists $\Delta H^{\ddagger}$, ΔH°, $\Delta S^{\ddagger}$ and ΔS° for oxides in which cation vacancies
are supposed to be the major defect. Note that in the table ΔH° and ΔS°
refer to the formation of 1 mole of vacancies so that in the case of Cu_2O
ΔH° is <u>one half</u> of the heat of solution of a gram atom of oxygen. This
arises quite simply as in Cu_2O there are two cation sites for each oxygen
site.

Referring to Table 2, it can be seen that $\Delta S^{\ddagger}$ is small. This is to be
expected for diffusion by a point defect mechanism involving very few atoms
in the elementary jump process. For the isomorphous series of monoxides,
$\Delta H^{\ddagger}$ varies only very little; this is a valuable confirmation of the correct-
ness of the assumption that diffusion is by the same mechanism in all these
oxides.

Turning now to the quantities for formation of a vacancy, it may be
seen that, in contrast to $\Delta H^{\ddagger}$, ΔH° varies very dramatically, and it is
instructive to see why this should be so.

We consider vacancies to be formed by the overall reaction (5) (this
is confirmed by the oxygen pressure dependence of c_i found for CoO). Now
in terms of the 'real' charges in the crystal $M^{2+}O^{2-}$ reaction (5) is

$$M_M^{2+} + 1/2\ O_2 \longrightarrow O_O^{2-} + V_M^{+} + M_M^{3+} \tag{5'}$$

which may be broken down into the following steps:

$$\text{(a)} \quad M_M^{2+} \longrightarrow V_M + M_{gas}^{2+}$$

$$\text{(b)} \quad 2e^{-} + 1/2\ O_2 \longrightarrow O^{2-}_{gas}$$

$$\text{(c)} \quad M_{gas}^{2+} + O_{gas}^{2-} \longrightarrow M_M^{2+} + O_O^{2-}$$
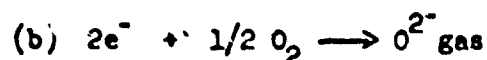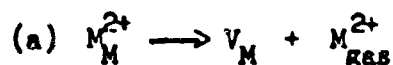
Table 2

Thermodynamic quantities for formation and migration of defects in several oxides

Oxide	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔH°	ΔS°
MnO[a]			0	
FeO	30		-28	
CoO	27	-0.8	10	-12
NiO	23	(-1)	40	(-14)
Cu_2O	12	-1.5	22	4.9

Note: Enthalpies in kcal mole^{-1}, Entropies in cal deg^{-1} mole^{-1}.

[a] reference (100)

(d) $V_M \longrightarrow V_M^+ + e^-$

(e) $M_M^{2+} \longrightarrow M_M^{3+} + e^-$
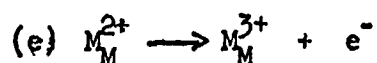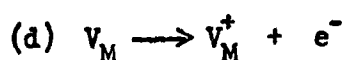
For the closely related series of oxides MnO, CoO, FeO, NiO, the energy involved in each of the steps (a) - (d) would be expected to vary only slightly. On the other hand step (e) is the ionization of M^{2+} and the energy for this step will vary considerably from atom to atom (ranging from 30.6 eV for Fe to 36.2 eV for Ni). It is expected, therefore, that the variation in ΔH° will be mirrored in the variation of the third ionization potential of the cation. Figure 1 shows that this is indeed the case. It can be seen that this type of non-stoichiometry is unlikely for MgO, as the third ionization energy of Mg is very high (80.1 eV)[*].

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[*]Because of this high ionization energy, one would expect in fact that a hole in MgO would be localized on an oxygen ion (rather than on Mg^{2+}). This appears to be observed in electron spin resonance.[16]

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Finally it should be remarked in this connection that the evaluation of c_1 requires the assumption that one type of defect predominates in the material. However Roth[17] has shown that in FeO there is an appreciable concentration of interstial iron, so that reaction (5) should possibly be replaced by a reaction such as

$$1/2 \ O_2 \longrightarrow O_o + Fe_i^{\bullet\bullet} + 2V_{Fe}'' + 2h^\bullet \tag{16}$$
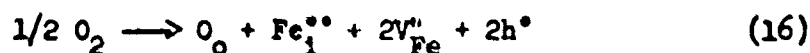
How far this observation affects the interpretation of results for oxides such as CoO, NiO and Cu_2O (in all of which the predominant defect is assumed to be cation vacancies) is not known. It is worth noting, however,

that for molten salts of the alkali halides there is good evidence for inter-stitial (in the sense of tetrahedrally coordinated) cations.[18]

It should also be mentioned that information about D_i may also be ob-tained directly, from the kinetics of annealing of a crystal containing a non-equilibrium concentration of defects. An example is to be found in the work of Thomas,[19] who measured the decay of conductivity of ZnO contain-ing an excess of interstitial zinc. Zinc is supposed to dissolve in zinc oxide according to

$$Zn \longrightarrow Zn_I^{\bullet} + e' \tag{17}$$

so that the conductivity is proportional to the concentration of excess zinc in the crystal and the rate of change of conductivity is proportional to the rate of diffusion of $Zn_I^{\bullet}$.

This type of experiment involves diffusion in a concentration gradient (i.e. interdiffusion) - a topic to which we return below.

Type C

A large number of oxides and sulfides exhibit a wide range of non-stoichiometry. Formerly, this was described in terms of point defects as for materials of type B. However, detailed studies of individual systems have frequently revealed the existence of a number of closely related phases of definite composition. Particularly notable are the x-ray studies of Magneli and his school and the phase equilibria studies of Eyring and co-workers. Examples of such phases are: TiO_{2n-1} with n = 4-10 known,[20] and WO_{3-x} and MoO_{3-x} which form a large number of phases of composition M_nO_{3n-2} and M_nO_{3n-1}.[21] An extreme example is $W_{20}O_{58}$ ($WO_{2.9}$).[22] Rare earth oxides in the range M_2O_3 - MO_2 afforded another example in which the existence of a number of stable phases of definite stoichiometry M_nO_{2n-2}

has been established.[23]

These results are not surprising as appears on first sight. Some time ago Bertaut[24] pointed out that, from considerations of electrostatic energy, a structure with a large concentration of vacancies would be expected to be very unstable with respect to an ordered phase. Indeed the possibility of existence of a very non-stoichiometric compound has recently been questioned.[1]

It is profitable to examine the situation in a little more detail. Figure 2a shows a two-dimensional crystal of nominal composition AB. A few A atoms have been removed, and clearly those empty A sites should now be referred to as A vacancies. Suppose now that 50% of the A atoms were removed in a systematic way giving a compound AB_2. This process has been almost completed in Figure 2b; it can be seen that some of the sites that were A sites in AB are interstitial sites in AB_2. So far there is no difficulty.

Let us now make a solid solution of AB and AB_2 such as shown in Figure 2c. It is not clear any longer whether we should refer to this as AB with A vacancies or AB_2 with interstitial A. However, as mentioned above, it is in fact rather unlikely that we should have a random solid solution of this type; the reasoning is as follows.

Referring again to Figure 2b, it can be seen that each interstitial A ion has four nearest neighbor A ions--a configuration that might be expected to be rather unfavorable for electrostatic reasons. Magneli[25] has pointed out that the same stoichiometry can be maintained and yet have no more than two nearest neighbor A ions for any given A ion. This can be done as shown in Figure 3a which is taken from Magneli's paper.[25] The feature to note now is that most of the ions in the crystal have the same immediate environment as in pure AB_2; the exceptional ions are arranged along zig-zag lines that run through the crystal. Thus, there are regions of pure AB_2 separated by randomly aligned regions of different stoichiometry (richer in A).

Adjacent AB_2 regions are no longer in phase, and to this extent there is strictly no longer long range order in the crystal. However, if the perfect AB_2 regions are sufficiently large, the x-ray diffraction pattern of the non-stoichiometric compound will be that of AB_2.

We enquire now as to ionic mobility in a crystal of this type. It is assumed that it is a very unfavorable configuration when an A has more than two A nearest neighbors, so that jumps that result in this type of configuration will not occur. This rule severely limits the number of A ions that can move at any one time. Figure 3b has been obtained by moving two ions that can move with the above restriction; it can be seen that in the new arrangement, ions that were previously unable to move can now do so. Eventually all the A ions will be able to jump, but the number able to jump at any one time will be rather small. In this sense the number of defects is rather small--much.smaller than the number of "vacancies" in the crystal.

Figure 3c, also after Magneli, shows how phases of general formula A_nB_{2n-1} can be built up. This is done very simply by allowing the zig-zag lines of extra atoms to line up in an ordered way throughout the crystal. The phase shown is A_5B_9 and is a stoichiometric compound that (as drawn) contains no defects at all. The real three dimensional phases mentioned earlier are no doubt much more complicated than the two dimensional case considered here; in particular both cations and anions will be involved in the ordering process.

To summarize the discussion so far· In a crystal AB_{n-x} having a structure (as revealed by x-ray diffraction) similar to AB_n, the stoichiometry may not be a reliable guide to the number of defects able to diffuse. For example, a vacancy should be defined as a site such that if an atom jumps into that site the energy of the crystal is unchanged. In this sense the number of

vacancies may be much less than the stoichiometric deficiency.

The example we considered in Figure 3a is still a non-stoichiometric crystal (in contrast to that shown in Figure 3c). It is well known, however, that we may have a stoichiometric compound with the same sort of requirements, namely that a given ion has a definite number of nearest neighbors, but in which there is no long range order. A very well known example is that of ice. Newman[26] has successfully interpreted the structure of Ga_2S_3 and related compounds from this point of view. Superficially these compounds have a defective ZnS structure, but Newman showed that each ion in the crystal has a definite coordination, just as in ice each oxygen has two hydrogen nearest neighbors. As Kroger[27] has pointed out, only deviations from the 'ideal' short-range order in which a given ion has a different number of nearest neighbors should be considered a defect in the Frenkel and Schottky sense. This might well be the case in TiO[28] and VO[29] for which at the stoichiometric composition the formula based on a rock salt structure is $M_{0.85}O_{0.85}$. A possible explanation is that each metal and each oxygen has 5 nearest neighbors (rather than six as in the perfect rock salt structure). Migration of (say) oxygen to a neighboring site requires that one metal will have four oxygen neighbors and one metal six neighbors. These 'defects' can then migrate through the crystal.

The only relevant diffusion work known to the author is that of Condit and Birchenall on $Fe_{1-\delta}S$.[30] These authors found a non-linear dependence of the iron diffusion coefficient on the degree of non-stoichiometry, δ; viz.

$$D_{Fe} = 0.16 \left\{ \delta^2 + 10^{-2} \exp (-4/RT) \right\}^{1/2} \exp \left\{ - (19 + 20\delta)/RT \right\} \qquad (18)$$

Although ordering of defects at a composition near Fe_7S_8 reduced the iron diffusion coefficient, the effect was less than one order of magnitude

change in D_{Fe}. It appears to the present author that this is strong evidence for short-range order above the disordering temperature. The complicated dependence of L on δ (which might naively be equated to iron vacancy concentration) defeats attempts at a simple explanation based on a random distribution of vacancies.

Finally under the heading of type C materials we should perhaps include compounds such as Cu_2S and Ag_2S in which an almost random distribution of ions over a number of lattice sites occurs, although the stoichiometry may be nearly perfect. In Cu_2S the copper atoms are in three sites occupied about 87%, 35% and 17% respectively.[31] This is to be compared with a completely random distribution in which 33% of each site would be occupied. In the high temperature form of Ag_2S the silver is thought to be randomly distributed.[32] Allen and Moore[33] found an extraordinarily high diffusion coefficient for silver in this phase, viz.

$$D_{Ag} = 2.8 \times 10^{-4} \exp (-3450 \text{ cal/RT}) \tag{19}$$

$\Delta S^{\ddagger}$ calculated from equation (3), and using a correlation factor $f = 0.50$,[34] is very close to zero. This is consistent with a model in which silver is able to move without creating any additional disorder. Allen and Moore comment further that the D_{Ag} is comparable with that calculated for a gas of silver atoms at the same temperature and density. Here, then, is one case where complete randomness is likely.

Oxygen Diffusion

In nearly all oxides except those of formula MO_2 (and possibly higher oxides) oxygen diffusion is considerably less rapid than cation diffusion (PbO is one exception). This situation is paralleled by that obtaining for the halides in which cation mobility is normally greater in the lower halides

but anion mobility greater in MX_2.[35] [36] In CdO and TiO_2 it appears that anion diffusion occurs by a vacancy mechanism, but for ZnO, Cu_2O, MgO, NiO and PbS it has been suggested on the basis of the pressure dependence of the diffusion coefficient that an interstial mechanism is operating. An alternative explanation was offered by Moore[37] and more recently reviewed by Woodbury.[38] This theory invoked cooperation of cation vacancies in anion diffusion and would provide an explanation of the observed dependence of D on a positive power of oxygen pressure. It does not appear possible to distinguish between these mechanisms at this stage, although in some instances a general indication of the mechanism of oxygen diffusion can be obtained from the magnitude of the pre-exponential factor in the diffusion coefficient.

Thus, writing $D = D_0 \exp(-E_0/RT)$ we see from equation (1), (2) and (3)

$$D_0 = (kT/h) \, a^2 \, \exp\left\{(\Delta S^\ddagger + \Delta S^\bullet)/R\right\}$$

$(kT/h) \, a^2$ is typically about 10^{-2} cm^2 sec^{-1} at 1000°C, and $\Delta S^\ddagger$ is generally expected to be rather small for diffusion by a point defect mechanism,[51] so that if D_0 is very different from 10^{-2} cm^2 sec^{-1} it will be due to the factor $\exp(\Delta S^\bullet/R)$.

For experiments at constant oxygen (or sulfur) pressure we can estimate the order of magnitude of $\Delta S^\bullet$ as follows. If oxygen vacancies are formed by a reaction such as

$$2O_O \longrightarrow 2V_O + O_2 \tag{20}$$

ΔS will be large and positive including not only the contribution from the gaseous oxygen (60.4 cal deg^{-1} $mole^{-1}$ at 1300°K), but also from the general loosening of the lattice in the proximity of the vacancy. This might contribute a factor of as much as $\exp(40 \text{ e.u}/R \sim 10^9$ to the pre-exponential

factor D_o. On the other hand formation of interstitials by e.g.

$$2V_I + O_2 \longrightarrow 2O_I \qquad (21)$$
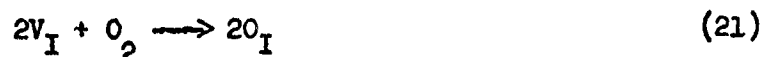
will be expected to have a negative ΔS with exp $(\Delta S/R)$ perhaps $\sim 10^{-5}$.

Compare for example (from Table 2), D_o for oxygen diffusion in MgO which

is thought to occur by an interstial mechanism[39] with D_o for oxygen

diffusion in CdO, which almost certainly proceeds by a vacancy mechanism.[40]

Finally, in connection with the subject of oxygen diffusion, it is very

interesting to note that recent measurements of xenon diffusion in several

ceramic oxides[41] gave results surprisingly similar to those obtained for

oxygen. While this may be fortuitous, one is lead to speculate on possible

mechanisms of diffusion in which molecular oxygen (which is similar in size

to zenon) plays a role. Clearly, more experiments of this type would be

very valuable.

Interdiffusion and Reaction

We have so far considered only self diffusion in a homogeneous crystal

as measured for example by tracer experiments. However, for many appli-

cations of interest to the chemist and ceramist it is interdiffusion, with

possible reaction to form a new phase, that is of interest.

Reactions between solid oxides to form new phases and gas solid re-

actions are the subject of a later paper so that they will be omitted here,

the present discussion being limited to two types of interdiffusion process.

These are (a) the interdiffusion of one component of a binary compound and

the compound itself (e.g. O_2 and Cu_2O) resulting in a change of stoichiometry

and (b) the interdiffusion of two oxides to form a solid solution of the

same structure (e.g. CoO and MgO).

The new features that we have to consider are that now we are concerned

with diffusion in a concentration gradient and the interdiffusion process will involve a flux of at least two different species. Until the advent of isotope tracer techniques, this was of necessity the only type of diffusion studied.

Formally, the rate of interdiffusion of A and B is characterized by an interdiffusion coefficient, given by[42]

$$\tilde{D} = c_A D_B + c_B D_A \tag{22}$$

where c_A, c_B are the mole fractions of A and B, and D_A and D_B are the diffusion coefficients of A and B in the solution of A and B. It may be shown that[42]

$$D_B = D_B^* \ (1 + d\ln\gamma_B/\partial\ln c_B)$$
$$D_A = D_A^* \ (1 + d\ln\gamma_A/d\ln c_A) \tag{23}$$

Where in turn D_A^*, D_B^* are the diffusion coefficients of A and B as measured in a homogeneous solution of A and B by, for example, tracer methods (i.e. in the absence of a chemical concentration gradient). γ_A is the activity coefficient of A in the solution.

For a binary solution from the Gibbs-Duhem equation we have that

$$\frac{\partial\ln\gamma_A}{\partial\ln c_A} = \frac{\partial\ln\gamma_B}{\partial\ln c_B} \equiv \frac{\partial\ln\gamma}{\partial\ln c} \tag{25}$$

so that from (22) we have the Darken Equation:[*]

$$\tilde{D} = c_A D_B^* + c_B D_A^* \ (1 + d\ln\gamma/d\ln c) \tag{26}$$

- -

[*] Strictly equation (26) is correct to the extent that there are no correlation effects and that there is no coupling between the flow of A and the concentration gradient of B and vice versa. For a more complete

expression for $\tilde{D}$ reference should be made to the review by Howard and Liddard[42].

- -

Turning now to some specific examples let us suppose that B is a gas that can dissolve in A forming a dilute solution. If A is considered a rigid matrix then $D_A \simeq 0$ and as the solution is dilute $c_A \simeq 1$ so that equation (23) becomes

$$\tilde{D} = D_B^* \ (1 + \partial \ln \gamma_B / \partial \ln c_B)$$

If B dissolves in A as ions by a reaction of the sort

$$B \longrightarrow B^{\nu+} + \nu e^- \tag{27}$$

Then using the well-known formalism of solution theory[43]

$$a_B = a_{\pm}^{\nu+1} = c_+ \gamma_+ \ c_-^{\nu} \gamma_-^{\nu} \tag{28}$$

where $a_{\pm}$ is the mean ionic activity and the +,- subscripts refer to $B^{\nu+}$ and e^- respectively. Assuming an ideal solution of $B^{\nu+}$ and e^- we have $\gamma_+ = \gamma_- = 1$ and $\nu c_+ = c_-$ so that

$$a_B = \nu^{\nu} \ c_B^{\nu+} \tag{29}$$

$$\partial \ln a_B / \partial \ln c_B = \nu + 1 \tag{30}$$

and thus

$$\tilde{D} = (\nu + 1) \ D_B^* \tag{31}$$

As an illustration we may take the diffusion of interstitial zinc in zinc oxide. We have seen that zinc dissolves in zinc oxide by the reaction

$$Zn_{gas} \longrightarrow Zn_I^{\bullet} + e' \tag{17}$$
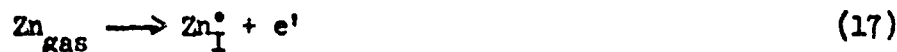
and the rate of uptake of zinc can be obtained from conductivity measurements.[19] In this example $\nu = 1$ so that

$$\tilde{D} = 2 \ D^* \ (Zn_I^{\bullet}) \tag{32}$$

Note that $D^*(Zn_I^\circ)$ is the rate of diffusion of interstitial zinc in homogeneous zinc oxide and is the defect diffusion coefficient, i.e. $D^*(Zn_I^\circ) = D_{Zn}/c(Zn_I^\circ)$ (cf equation (4)).

The type of diffusion just considered is more frequently discussed from a slightly different point of view.[44] As the electron is more mobile than the zinc ion it will tend to run ahead creating a 'diffusion potential' Φ that enhances the rate of diffusion (accounting for the factor of 2 in equation (32)). The flux of zinc ions of charge q is then given by

$$J(Zn_I^\circ) = -D^*(Zn_I^\circ) \quad dc(Zn_I^\circ)/dx + q \, d\Phi/dx \tag{33}$$

and the flux of electrons is similarly

$$J(e^-) = -D^*(e^-) \, dc(e^-)/dx - q \, d\Phi/dx \tag{34}$$

Electrical neutrality requires that

$$J(e^-) = J(Zn_I^\circ) \tag{35}$$

which together with the inequality

$$D^*(Zn_I) \ll D^*(e^-) \tag{36}$$

and $$\tilde{D} = D(Zn_I^\circ) = -J(Zn_I^\circ)/(dc(Zn_I^\circ)/dx)$$

yields equation (32). This type of diffusion is sometimes called <u>ambipolar diffusion</u>.

As a second example, we may consider the uptake of oxygen by a crystal MO. We suppose that oxygen is taken up by the reaction discussed earlier

$$1/2 \, O_2 \longrightarrow O_o + V_M' + h^\bullet \tag{5}$$
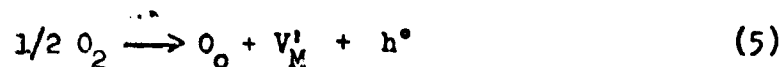
The mobile ionic species will now be the cation vacancy which we have assumed ionized as shown. In this instance we have

$$\tilde{D} = 2 \, D_V^* \tag{37}$$

where now D_V^* is the vacancy diffusion coefficient D_M/c_V.

An experiment of this type could readily be performed as follows. A crystal of MO at a low oxygen pressure could be suddenly subjected to greatly enhanced oxygen pressure (all the time staying within the field of existence of MO, of course). The rate of uptake of oxygen (measured by the change in gas pressure or perhaps gravimetrically) will then yield the vacancy diffusion coefficient directly. This is a method that deserves more attention than it has been accorded so far.

There has of necessity been a simplified account of interdiffusion for two simple examples. For a discussion of interdiffusion taking into account cation and anion mobility and Schottky equilibrium see Brebrick.[45]

We turn now to a second type of interdiffusion - that of two solids forming a solid solution. For simplicity the discussion will be limited to on greatly oversimplified example to illustrate the type of behavior to be expected. The example considered is that of two simple oxides AO and BO that have been placed together and allowed to interdiffuse.

After a diffusion anneal the interdiffusion coefficient may be obtained from a Matano[46] analysis from

$$\tilde{D} = \frac{1}{2t} \left.\frac{\partial x}{\partial c}\right/_c \int_c^o x \, dc \tag{38}$$

where the origin of x (the Matano interface) is defined so that

$$\int_o^1 x \, dc = o \tag{39}$$

$\tilde{D}$ measured in this way does not by itself give any information about the magnitude of D_A^* or D_B^*.

In order to find out what type of concentration-distance curve to expect we make the following simplifying assumptions.

It is assumed that oxygen diffusion is negligible and that cation diffusion is by a vacancy mechanism and further that the concentration of vacancies in pure AO is negligible compared with that in BO.

We have now that

$$D_A = D_{VA} \, c_V$$

$$D_B = D_{VB} \, c_V$$

$$(40)$$

where D_{VA}, D_{VB} measure the rate of vacancy diffusion by jump into an A or a B site respectively. It will not affect our general conclusions if we let $D_{VA} = D_{VB} = D_V$. We then have very simply

$$\tilde{D} = D_V \, c_V \tag{41}$$

c_V will depend strongly on the concentration of BO (C_B) in the solution; suppose

$$c_V = c_V^{\bullet} \, c_B^{\,n} \tag{42}$$

where n is a rational number of the order of unity. Thus from (41) and (42) if D_B° is the diffusion coefficient of B in pure BO:

$$\tilde{D} = D_V \, c_V^{\bullet} c_B^{\,n} = D_B^{\circ} c_B^{\,n} \tag{43}$$

The expected concentration profile for $\tilde{D}$ of this type can be obtained by numerical solution of Fick's equation.[47] Figure 4 shows the results for n = 2, 1 and 1/2. In this diagram c_B is plotted against the dimensionless parameter

$$\lambda = x/(4D_B^{\bullet}t)^{1/2} \tag{44}$$

The curves of Figure 4 are rather interesting. They show, for example, that the concentration of B will fall to zero at a finite distance into the AO so that there will be a definite rate of advance of the boundary of the

solid solution into AO. This rate is

$$dx/dt = \lambda_o (D_B^\circ/t)^{1/2} \tag{45}$$

where λ_o is the value of λ at which c_B falls to zero.

Although it involves some rather drastic approximations the above analysis probably described fairly well the general behavior of systems such as CoO-MgO and FeO-MgO. A recent study of the FeO-MgO system[48] did indeed show a concentration profile remarkably like that of figure (4) for n = 2. The CoO-MgO system[49] likewise shows a sharp boundary between (Co, Mg) O and pure MgO, but it should be emphasized that despite statements to the contrary[49] the rate of advance of the boundary is not a measure of the rate of diffusion of cobalt in MgO but (cf equation (45)) perhaps more nearly measures the rate of diffusion of cations in pure CoO.

A complete analysis of a system such as this presents a rather difficult problem, that has not yet been solved to the author's knowledge. One difficulty that might be mentioned is that except for the case of n = 1 (vacancy concentrations linearly dependent on concentration of B) the total number of cation sites is not constant. As a consequence it will in general be necessary for the solid system as a whole either to gain or to lose oxygen. This will be a particularly important effect for systems involving oxides such as FeO where the vacancy concentration is very large.

Diffusion Data

Finally we present in condensed form a summary of the data available on diffusion in oxides and sulfides. Only data directly measured by tracer or similar techniques have been included. No effort has been made to assess the reliability of any measurements, as this would be extremely difficult to do objectively. It must be pointed out, however, that in a few instances

where measurements have been made independently on the same system, widely differing results have been obtained. This is no doubt due partly to the problem of impurities mentioned earlier; however, some particularly troublesome anomalies remain. One notorious example is that of the diffusion of zinc in zinc oxide. Only two representative values are included in the table. For a survey of this problem, reference may be made to the paper of Moore and Williams[50] and the ensuing discussion[51].

In a great number of cases diffusion coefficients are measured in a constant atmosphere (frequently air) with temperature as the only parameter. D is then reported as

$$D = D_o \exp (- E/RT)$$

It is emphasized again here that it would frequently be very profitable also to make measurements in which the partial pressures of the ambient gases are systematically varied. Where this has been done it is noted in the table.

One might inquire as to whether there were any significant trends in the diffusion coefficients reported. Lindner[52] has made the interesting observation that for many oxides the cation diffusion coefficient at the melting point is within an order of magnitude of $10^{-7} cm^2 sec^{-1}$, but this rule is by no means universally true.

The enormous range of reported values for D_o and E calls for comment. There appears to be no direct correlation between D_o and F, although as might be expected, in general a large D_o is accompanied by large E. There is a more direct correlation between D_o and E/T_m; in figure 5, E/T_m is plotted against log D_o. It may be seen that there appears to be an approximately linear relation between these two quantities for the oxygen data, and a less direct correlation for cation diffusion.

These observations present an interesting theoretical challenge. Ubbelohde[53] has remarked on the very large pre-exponential factor in many rate processes in solids and was led to suggest that this might be related to a persistence of activation energy or 'overshoot' phenomenon. By this means an ion (particularly an interstitial) could jump several atomic distances at once. Alternatively one might envisage that, rather than diffusion by a point defect mechanism, there was a cooperative effect in which either a cluster or a plane in the crystal moved. For a recent discussion of the relationship between activation energy and pre-exponential factor and for further references see reference (54).

Acknowledgements

Solid	Diffusant	D_o $cm^2 sec^{-1}$	E_{kcal}	Comment	Reference
Cu_2O	Cu	4.4×10^{-2}	36.1		55
		0.12	37.8		56
	O	6.5×10^{-3}	39.3	$D \sim P_{O_2}^{1/2}$	57
	Ag	6×10^{-3}	27.6		58
	Zn	4×10^{-4}	30.0		59
MgO	Mg	.249	79		(60)
	O	2.5×10^{-6}	52.4	$D_o \sim P_{O_2}^{1/2}$	39, 61
	Fe	8.83×10^{-5}	41.7		62
	Co	5.78×10^{-5}	47.4		62
	Ni	1.80×10^{-5}	48.3		62
	Zn	1.48×10^{-5}	42.5		63
	Xe	$\sim 3 \times 10^{-6}$	~ 64		41
NiO	Ni	2×10^{-4}	39.6		64
		1.7×10^{-2}	56		65
	O	6.2×10^{-4}	57.5	$D_o \sim P_{O_2}^{1/2}$	66
ZnO	Zn	~ 10	73		67
		1.3×10^{-5}	43.5		50
	O	6.5×10^{11}	165		50
	In	2.5×10^{2}	73		68
FeO	Fe	1.4×10^{-2}	30.2	in $FeO_{1.087}$	69, 13
CoO	Co	2.15×10^{-3}	34.5	$D_o \sim P_{O_2}^{0.3}$	13
PbO	Pb	10^5	66.6		70
	O	5.39	22.4		71
CdO	O	8×10^6	93	$D \sim P_{O_2}^{-1/6}$	40
BeO	O		68		72
	Xe	$\sim 3 \times 10^{-6}$	~ 64		41

TABLE 2 (Continued)

Solid	Diffusant	D_o cm^{2}sec^{-1}	E_{kcal}	Comment	Reference
CaO	Ca	0.4	81		73
BaO	Ba	$\sim 10^{30}$	~ 275	above 1350°C	74
Al$_2$O$_3$	O	1.9×10^3	152	T > 1400°C	75
		6.3×10^{-8}	57.6	T < 1400°C	75
	Al	28	114		76
	Xe	3×10^{-6}	63.5		41
	Fe	9.2×10^{-8}	27.6		77
Cr$_2$O$_3$	Cr	4×10^3	100		78
	O	15.9	101		79
		.137	61		80
Fe$_2$O$_3$	Fe	4×10^5	112.0		81
		1.3×10^6	100		82
	O	10^{00}	146		83
Y$_2$O$_3$	Y	2.4×10^{-4}	43.9		84
UO$_2$	U	0.23 4.3×10^{-4}	104.6 88.0	H$_2$O atmosphere H$_2$ atmosphere	85 86
	others				36, 87
ZrO$_2$	O	5.1×10^{-3}	29.8	(15% CaO)	10
	Xe	6.5×10^{-8}	42		41
TiO$_2$	O	2×10^{-3}	60	(.01% Al$_2$O$_3$)	88
	Fe	2×10^{-2}	55.0	in air	77
		1.9×10^{-1}	55.4	in vacuum	77
SnO$_2$	Sn	10^6	119		78
GeO$_2$	O	10^{-7}	28.5		89
		(10^{-3})	27.5		90
Fe$_3$O$_4$	Fe	5.2	55.0	Fe$_{2.993}$O$_4$	69
		6×10^5	84	$D \sim P_{O_2}$ 0.4(9')	91

TABLE 2 (Continued)

Solid	Diffusant	D_0 cm^{2}sec^{-1}	E_{kcal}	Comment	Reference
$CaSiO_3$	Ca	7.4×10^4	112.0		81
$PbSiO_3$	Pb	85	59.5		81
$PbSiO_4$	Pb	8.2	47		81
$SrTiO_3$	O	$\sim 10^{-5}$	~ 27.5	independent of F_{O_2}	92
$ZnFe_2O_4$	Zn	8.8×10^2	86.0		93
	Fe	8.5×10^2	82		93
$ZnCr_2O_4$	Zn	60	85.5		78
$ZnCr_2O_4$	Cr	8.5	81.0		78
$CoCr_2O_4$	Co	10^{-3}	51		94
	Cr	2	72.5		94
$NiCr_2O_4$	Ni	1.5×10^{-3}	61.4		52
	Cr	74	72.5		78
	O	.017	65		63
$ZnAl_2O_4$	Zn	2.5×10^{-2}	78.0		78
$NiAl_2O_4$	Ni	2.9×10^{-5}	53.5		52
$SnZn_2O_4$	Sn	2×10^5	109		78
	Zn	37	76.3		78
$CaFe_2O_4$	Ca	30	86		81
	Fe	0.4	72		81
$Y_3Fe_5O_{12}$	O	0.4	65.4		95
Ag_2S	Ag	2.8×10^{-4}	3.5	in cubic Ag_2S	33
	S	2.4×10^{-4}	25	"	96
PbS	Pb	8.6×10^{-5}	35	stoichiometric PbS	97
	S	6.8×10^{-5}	31.5	"	94
FeS	Fe	see text equation (18)			30
	S	$10^{33 \pm 17}$	240		30

TABLE 2 (Continued)

Solid	Diffusant	D_o $cm^2 sec^{-1}$	E_{kcal}	Comment	Reference
NiS	Ni	1.1×10^{-2}	25.5	$\parallel$ c-axis	99
		8.5×10^{-3}	25.6	$\perp$ c-axis	
	S	2.5×10^{2}	65.5	$\parallel$ c-axis	99
		2.2×10^{6}	87.5	$\perp$ c-axis	
CdS	Cd	3.4	46	in sat. Cd Vapor	38

References

1. J. S. Anderson in <u>Nonstoichiometric Compounds</u>, Am. Chem. Soc. 1963.

2. see e.g. the calculations of J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan, 9, 944 (1954) for MgO, CaO and SrO.

3. J. E. Wertz, J. W. Orton and P. Auzins, J. Appl. Phys. 33, 332 (1962).

4. H. Kanzaki, K. Kido and T. Nino miya, J. Appl. Phys., 33, 482 (1962). H. Kanzaki, K. Kido and S. Ohzora, J. Phys. Soc. Japan, 18, Suppl. III, 115 (1963).

5. M. Tosi, Solid State Physics (F. Seitz and D. Turnbull, Eds.) 16, 1 (1964).

6. A. B. Lidiard in <u>Handbuch der Physik</u>, 20, 246, Springer-Verlag (1957).

7. K. Compaan and Y. Haven, Trans. Far. Soc., 52, 786 (1956).

8. T. P. Hoar and L. E. Price, Trans. Farad. Soc., 34, 867 (1938).

9. H. Schmalzried, Z. phys. Chem. (Frankfurt) 23, 87 (1963).

10. W. D. Kingery, J. Pappis, M. E. Doty and D. C. Hill, J. Am. Cer. Soc., 42, 393 (1959).

11. H. Peters and H. H. Mobius, Z. Phys. Chem., 209, 298 (1958). E. C. Subbarao, P. H. Sutter and J. Hrizo, Semiannual Tech. Rept., Contract Nonr - 3800, Sept. 1964.

12. S. P. Mitoff, J. Chem. Phys., 33, 941 (1960); 36, 1383 (1962). H. Schmalzried, J. Chem. Phys., 33, 940 (1960).

13. R. E. Carter and F. D. Richardson, Trans. A.I.M.E., 194, 1245 (1954).

14. M. O'Keeffe and W. J. Moore, J. Chem. Phys., 36, 3009 (1962).

15. A. E. Stearn and H. Eyring, J. Phys. Chem., 44, 955 (1940).

16. J. E. Wertz, P. Auzins, J. H. E. Griffiths and J. W. Orton, Disc. Farad. Soc., 28, 136 (1959).

17. W. L. Roth, Acta. Cryst., 13, 140 (1960).

18. D. M. Gruen, J. Chem. Phys., 41, 2569 (1964).

19. D. G. Thomas, J. Phys. Chem. Solids, 3, 229 (1957).

20. S. Andersson, B. Collen, U. Kuylenstierna and A. Magneli, Acta. Chem. Scand., 11, 1641 (1957).

21. L. Kohlborg in <u>Nonstoichiometric Compounds</u>, Am. Chem. Soc. (1963).

22. A. Magneli, Arkiv Kemi, $\underline{1}$, 513 (1949).

23. D. J. M. Bevan, B. G. Hyde and L. Eyring to be published. L. Eyring and B. Holmberg in Nonstoichiometric Compounds, Am. Chem. Soc. (1963).

24. E. F. Bertaut, J. Phys. Radium, $\underline{13}$, 372 (1958).

25. A. Magneli, Transition Metal Compounds (E. R. Schatz, Ed.) Gordon and Breach, N.Y. (1964) p. 109.

26. P. C. Newman, J. Phys. Chem. Solids, $\underline{23}$, 19 (1962).

27. F. A. Kröger, The Chemistry of Imperfect Crystals, North Holland (1964) p. 414.

28. S. P. Denker, J. Phys. Chem. Solids, $\underline{25}$, 1397 (1964).

29. M. Hoch and D. Ramakrishnan, J. Phys. Chem. Solids, $\underline{25}$, 869 (1964).

30. R. H. Condit and C. E. Birchenall, AFOSR report TN60-245 (1960).

31. B. J. Wuensch and M. J. Buerger, Min. Soc. Am. Special paper 1 (1963).

32. P. Rahlfs, Z. Phys. Chem., $\underline{B31}$, 157 (1936).

33. R. L. Allen and W. J. Moore, J. Phys. Chem., $\underline{63}$, 223 (1959).

34. W. J. Moore, J. Chem. Ed., $\underline{38}$, 232 (1961).

35. A. B. Lidiard in Handbuch der Physik, $\underline{20}$, 246, Springer-Verlag (1957).

36. H. Matzke and R. Lindner, Z. Naturforsch, $\underline{19a}$, 1178 (1964).

37. W. J. Moore, Y. Ebisuzaki and J. A. Sluss, J. Phys. Chem., $\underline{62}$, 1438 (1958).

38. H. H. Woodbury, Phys. Rev., $\underline{134}$, A492 (1964).

39. M. O'Keeffe and W. J. Moore, Report to U.S.A.E.C. Contract At-(11-1)-250 (1961).

40. R. Haul and D. Just, J. Appl. Phys., $\underline{33}$, 487 (1962).

41. D. L. Morrison, S. Elleman and D. N. Sunderman, J. Appl. Phys., $\underline{35}$, 1616 (1964).

42. L. S. Darken, Trans. AIME, $\underline{175}$, 184 (1948).
    R. E. Howard and A. B. Lidiard, Reps. Progr. Phys., $\underline{27}$, 161 (1964).

43. see e.g. W. J. Moore, Physical Chemistry, Prentice Hall, N.J. (1963) p. 346.

44. N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Oxford 1940, p. 256.

45. R. Brebrick, J. Appl. Phys., $\underline{30}$, 811 (1959).

46. C. Matano, Japan. J. Phys., $\underline{8}$, 109 (1933).
    W. Jost, Diffusion in Solids, Liquids, Gases, Academic Press (1960) p. 31.

47. W. Kass and M. O'Keeffe, to be published.

48. E. B. Rigby and I. B. Cutler, J. Am. Cer. Soc., $\underline{48}$, 95 (1965).

49. I. Zaplatynsky, J. Am. Cer. Soc., $\underline{45}$, 28 (1962); J. Appl. Phys., $\underline{35}$, 1358 (1964).

50. W. J. Moore and E. L. Williams, Disc. Far. Soc., $\underline{28}$, 86 (1959).

51. G. Heiland and E. Mollwo, Disc. Far. Soc., $\underline{28}$, 123 (1959).

52. R. Lindner, Proc. 2nd Int. Conf. Peaceful Uses Atomic Energy, $\underline{20}$, 116 (1958).

53. A. R. Ubbelohde, Disc. Far. Soc., $\underline{23}$, 128 (1957).

54. P. Ruetschi, Z. Phys. Chem. (N.F.), $\underline{14}$, 277 (1958).

55. W. J. Moore and B. Selikson, J. Chem. Phys., $\underline{19}$, 1539 (1951).

56. K. Hauffe, Reactionen in und an Festen Stoffe, Springer (1955).

57. W. J. Moore, Y. Ebisuzaki and J. Sluss, J. Phys. Chem., $\underline{62}$, 1438 (1958).
    M. O'Keeffe, Y. Ebisuzaki and W. J. Moore, J. Phys. Soc. Japan, $\underline{18}$, Suppl. II, 131 (1963).

58. A. I. Andrievskii, A. V. Sandulova and M. T. Yaskevich, Sov. Phys. Solid State, $\underline{2}$, 581 (1960).

59. idem. Sov. Phys. Solid State, $\underline{2}$, 800 (1960).

60. R. Lindner and G. D. Parfitt, J. Chem. Phys., $\underline{26}$, 182 (1957).

61. Y. Oishi and W. D. Kingery, J. Chem. Phys., $\underline{33}$, 905 (1960).

62. B. J. Wuensch and T. Vasilos, J. Chem. Phys., $\underline{36}$, 2917 (1962).

63. B. J. Wuensch and T. Vasilos, U. S. Govt. Rept. AD-611814 (1963).

64. J. S. Choi and W. J. Moore, J. Phys. Chem., $\underline{66}$, 1708 (1962).

65. R. Lindner and Å. Åkerstrom, Disc. Far. Soc., $\underline{23}$, 133 (1957).

66. M. O'Keeffe and W. J. Moore, J. Phys. Chem., $\underline{65}$, 1438 (1961).

67. R. Lindner, Acta. Chem. Scand., $\underline{6}$, 457 (1952); E. A. Secco and W. J. Moore, J. Chem. Phys., $\underline{26}$, 942 (1957).

68. D. G. Thomas, J. Phys. Chem. Solids, $\underline{9}$, 31 (1959).

69. L. Himmel, R. F. Mehl and C. E. Birchenall, Trans. A.I.M.E., 197, 1250 (1953).

70. R. Lindner and H. N. Terem, Arkiv. Kemi, 4, 385 (1952).

71. B. A. Thompson and R. L. Strong, J. Phys. Chem., 67, 594 (1963).

72. Unpublished work of J. B. Holt quoted in ref. 32.

73. R. Lindner, St. Astrümdal and Å. Åkerstrom, Acta. Chem. Scand., 6, 468 (1952).

74. R. W. Redington, Phys. Rev., 87, 1016 (1952).

75. Y. Oishi and W. D. Kingery, J. Chem. Phys., 33, 480 (1960).

76. A. E. Paladino and W. D. Kingery, J. Chem. Phys., 37, 957 (1962).

77. V. Izvekov and K. Gorbunova, quoted by B. I. Boltaks, Diffusion in Semiconductors, Academic Press (1963).

78. R. Lindner and Å. Åkerstrom, Z. Phys. Chem. (Frankfurt), 6, 162 (1956).

79. W. Hagel, J. Am. Cer. Soc., 48, 70 (1965).

80. W. C. Hagel and A. U. Seybolt, J. Electrochem. Soc., 108, 1146 (1961).

81. R. Lindner, Z. Naturforsch., 10a, 1027 (1955).

82. V. I. Izvekov, N. S. Gorbunov and A. A. Babad-Zakhryapin, Physics and Metallography, 14, 30 (1963).

83. W. D. Kingery, D. C. Hill and R. P. Ne son, J. Am. Cer. Soc., 43, 473 (1960).

84. M. F. Berard and D. R. Wilder, J. Appl. Phys., 34, 2318 (1963).

85. R. Lindner and F. Schmitz, Z. Naturforsch., 16a, 1373 (1961).

86. J. Belle, A. B. Auskern, W. A. Bostrom and F. S. Susko, Reactivity of Solids (J. H. de Boer Ed.), Elsevier (1960).

87. Sr, Ru, Ce, Cs: N. Oi and J. Takagi, Z. Naturforsch., 19a, 1331 (1964), Zr, Y, Pm: F. Schmitz and R. Lindner, Z. Naturforsch., 16a, 1096 (1961).

88. R. Haul and D. Just, J. Phys. Chem. Solids, 26, 1 (1965).

89. T. Tolenda and W. D. Kingery, J. Appl. Phys., 34, 2014 (1963).

90. J. Denoncin and V. Garino-Canina, Comptes Rend., 250, 1815 (1960).

91. S. M. Klotsman, A. N. Timofeyev and I. Sh. Traktenberg, Fiz. Metal i Metallov., 10, 732 (1960).

92. A. E. Paladino, L. G. Rubin and J. S. Waugh, J. Phys. Chem. Solids, 26, 391 (1965).

93. R. Lindner, Acta. Chem. Scand., $\underline{6}$, 457 (1952); Z. Elektrochem., $\underline{59}$, 967 (1955).

94. R. Sun, J. Chem. Phys., $\underline{28}$, 290 (1958).

95. A. E. Paladino, E. A. McGuire and L. G. Rubin, J. Am. Cer. Soc., $\underline{47}$, 280 (1964).

96. M. Ishiguereo, F. Oda and T. Fujino, Mem. Inst. Sci. Indus. Res. Osaka Univ., $\underline{10}$, 1 (1953) quoted in ref. 33.

97. G. Simkovich and J. B. Wagner, J. Chem. Phys., $\underline{38}$, 1368 (1963).

98. M. S. Seltzer and J. B. Wagner, J. Phys. Chem. Solids, $\underline{26}$, 233 (1965).

99. S. M. Klotsman, A. N. Timofeyev and I. Sh. Trakhtenburg, Fiz. Metal i Metallov., $\underline{16}$, 743 (1963).

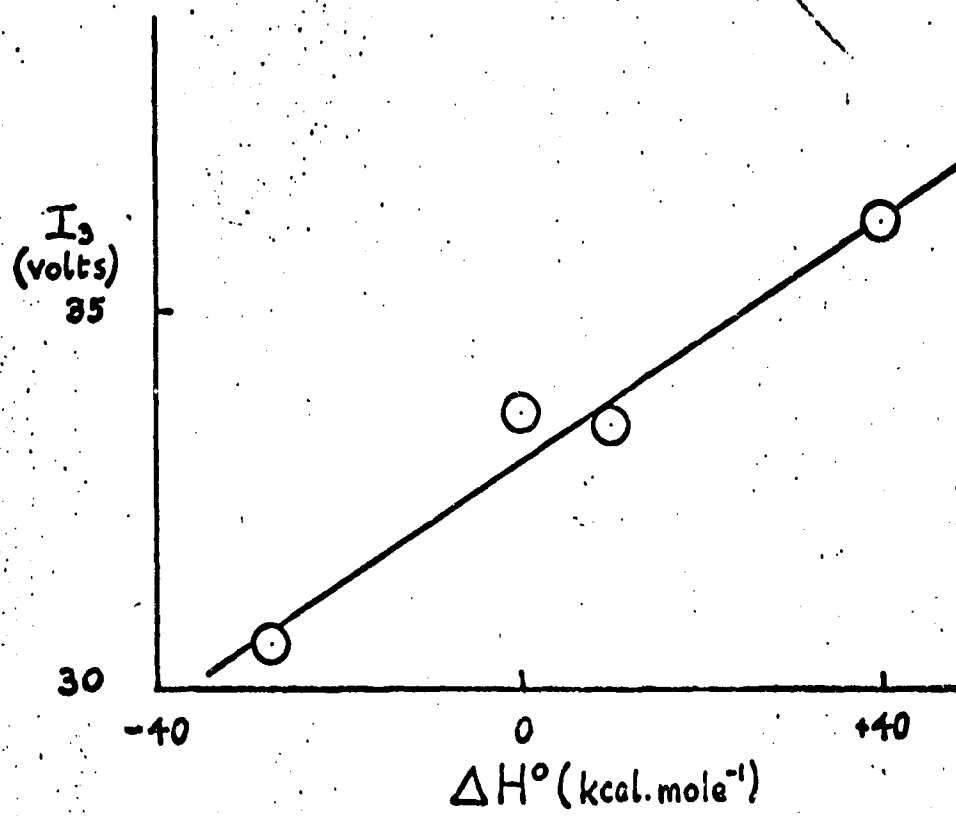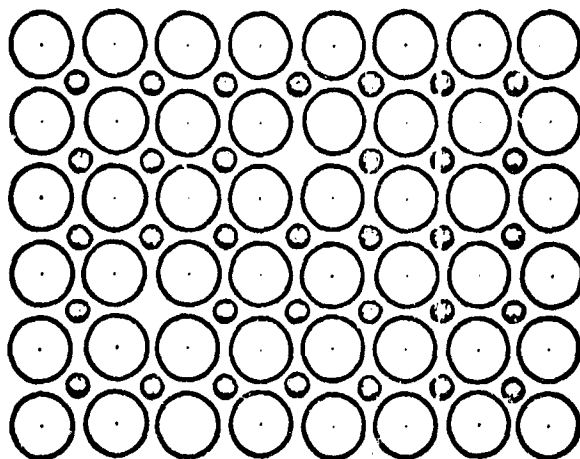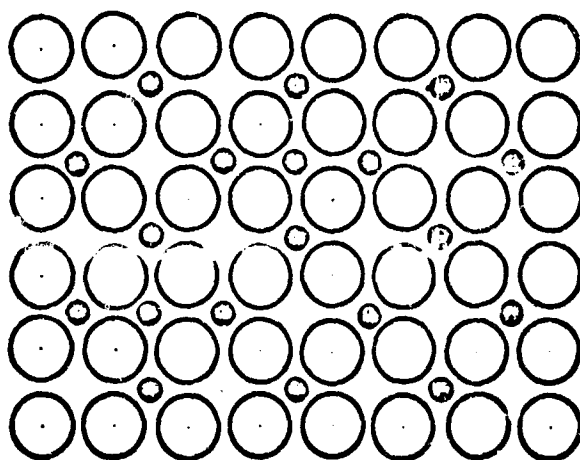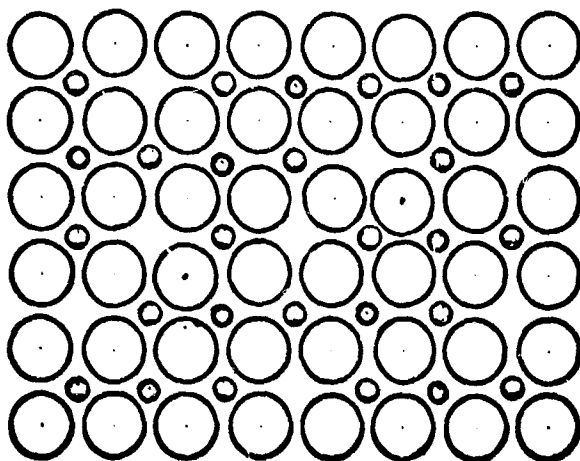100. M. W. Davies and F. D. Richardson, Trans. Far. Soc., $\underline{55}$, 604 (1959).

FIGURE 1

AB with vacancies

AB_2 with interstitials

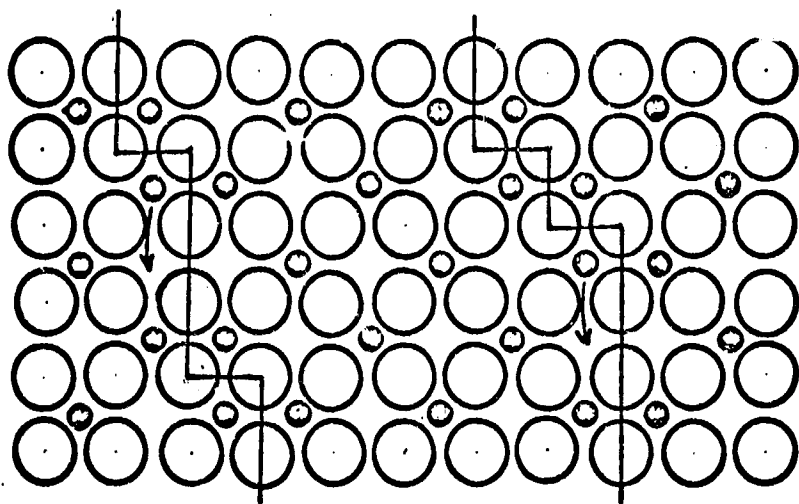AB_{2-x} or AB_{1+x}

FIGURE 2   ● A   ○ B

A

B

C

FIGURE 63

FIGURE 4

$$\lambda = x/(4D_o t)^{1/2}$$
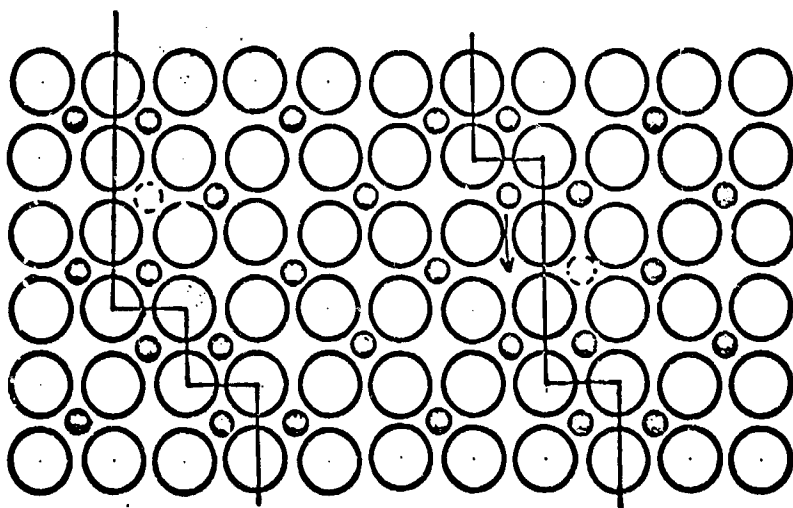
FIGURE 5

Chemical Diffusion in Wüstite (FeO$_x$)

R. H. Campbell and M. O'Keeffe
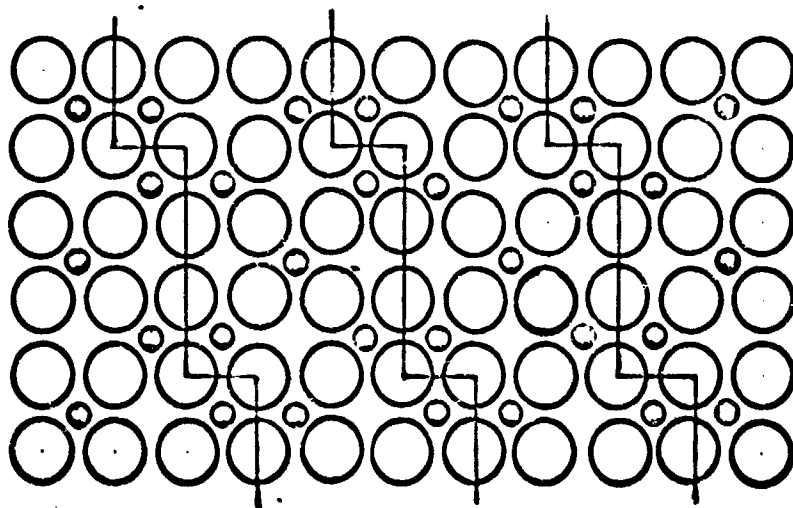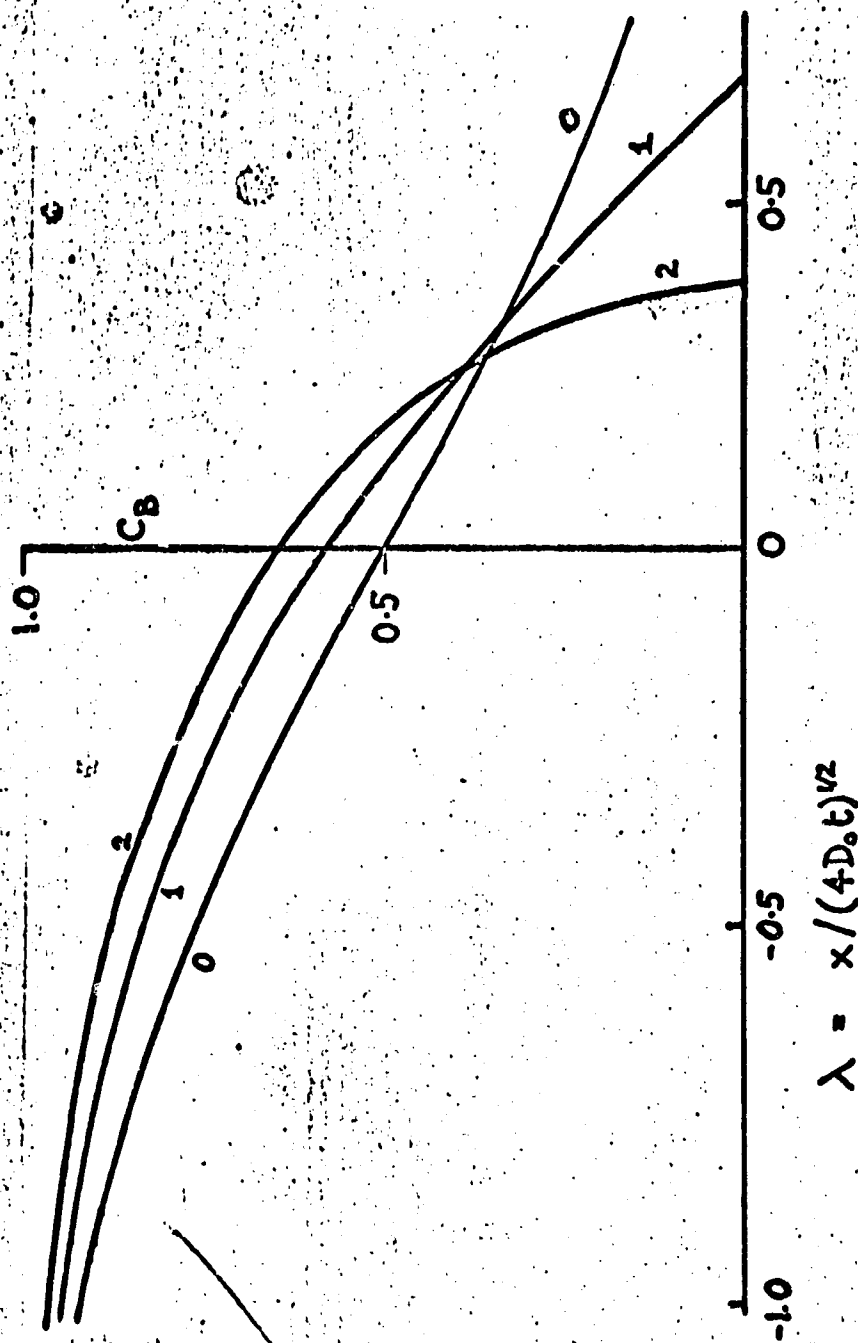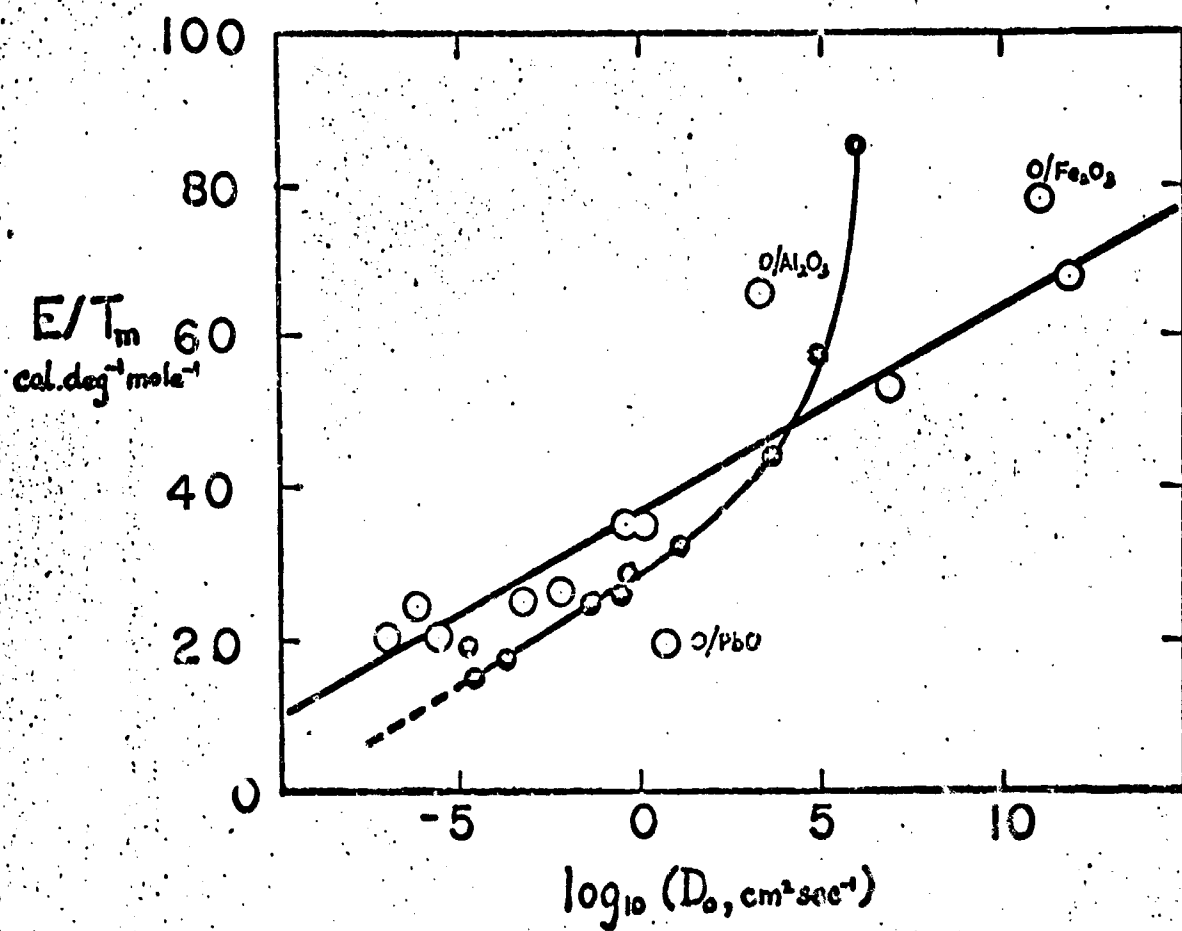
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Introduction

A large number of chemical reactions of considerable industrial importance involve the diffusion controlled transport of matter in oxides. As examples we may cite the oxidation of metals, the reduction of oxides, sintering of ceramics and the formation of ternary oxides (such as spinels) from binary oxides. It is clearly of considerable interest to be able to relate the diffusion coefficients characterizing these processes to the diffusion coefficients obtained from radio-isotope studies in homogeneous materials.

In order to clarify the definitions used and also to make clear the under-lying assumptions, we first sketch a derivation of the relationship between the 'chemical' and 'tracer' diffusion coefficients, following the general treatment given for example by Darken.[1]

In an experiment in which a net flux of matter is observed, a chemical diffusion coefficient can be defined in terms of the experimentally measured quantities by Fick's equation

$$\widetilde{D}_i = -J_i/\mathrm{grad}\ c_i \tag{1}$$

In practice an integrated form of Fick's 'second' equation is usually used but this is equivalent   the definition (1).

To relate $\widetilde{D}$ to other measurable quantities it is assumed that the driving force for isothermal diffusion is the gradient of electrochemical potential μ so that the velocity of the diffusing species i is

$$V_i = J_i/c_i = -u_i\ \mathrm{grad}\ \mu_i \tag{2}$$

where u_i is the mobility of species i. Writing

$$\mu_i = \mu_i{}^o + RT\ \ln a_i \tag{3}$$

we have from eqs. (1) and (2)

$$\tilde{D}_i = u_i\, RT\, (d\ln a_{\pm}/d\ln c_i) \tag{4}$$

In order to relate $\tilde{D}_i$ to the tracer diffusion coefficient, D_i^*, it is supposed that in a dilute solution the tracer atom behaves identically to the solvent atoms and that $d\ln a_i/d\ln c_i$ is unity. However it is possible that atomic jumps are not completely random but correlated so that we write

$$D_i^* = f\, u_i\, RT \tag{5}$$

where f is correlation factor. We return to a discussion of f below. Substitution of eq. (5) into eq. (4) yields finally the Darken equation

$$\tilde{D}_i = (1/f)\, D_i^*\, (d\ln a_i/d\ln c_i) \tag{6}$$

Wüstite (FeO_x) would appear to be an ideal material with which to test eq. (6). It has been known since the experiments of Pfeil[2] that oxygen diffusion is negligibly small in this phase. Several concordant measurements of tracer diffusion have been made[3,4,5]; the results of some of these measurements are hown in Figure 1. It has also been shown[3,5] that D_{Fe}^* increases with increasing x in FeO_x especially at higher temperatures (above $900°C$); this is a significant observation to which we return below.

There have also been a number of measurements[6,7,8] of activity as a function of concentration which are again in good agreement with each other. From these we have calculated that at $1050°C$ in FeO_x

$$d\ln a_{Fe}/d\ln c_{Fe} = 28.5\, x^2 \tag{7}$$

Levin and Wagner[9] studied chemical diffusion in this system by partial reduction of FeO_x. Their results were in fair accord with eq. (6) but interestingly it was found that $\tilde{D}$ decreased with increasing x whereas, if f is constant,

eq. (6) predicts an increase of $\tilde{D}$ with x (both D_{Fe}^{*} and $d\ln a_{Fe}/d\ln c_{Fe}$ increase with increasing x).

We decided to examine this system a little more closely, to see whether we could resolve this discrepancy; as will be seen our results are in even less accord with eq. (6).

Experimental

FeO_x was made in situ in a vacuum microbalance apparatus by oxidizing 1 mm thick 99.999% (with respect to metallic impurities) iron from United Mineral and Chemical Corp. in an approximately equimolar CO_2/CO mixture. The material was always maintained within the field of stability of wüstite after oxidation. Examination of the specimen after a series of experiments showed that it was coarsely crystalline with grains several mm in size and with a hollow core resulting from the outward diffusion of iron during oxidation. After equilibration in a given CO_2/CO mixture the pressure was reduced to less than 1 mm (oxygen activity being unchanged during this process). A CO_2/CO mixture of slightly different oxygen activity was then added and the kinetics of oxygen uptake or loss by the sample was followed. The diffusion coefficient was calculated utilizing the well-known solution[9] for this diffusion problem from the data for the last 50% of the weight change. The total weight change was typically several tenths of a milligram and could be measured with a precision exceeding 1%. It is characteristic of this type of measurement that only relative weight changes need be measured but in fact the absolute weight changes agreed well with the published data.[6,7,8] The thermocouple was calibrated in situ by observing the melting point of a sample of pure gold hanging in place of the sample.

Results

Most of the measurements were confined to constant temperature of 1055°C.
Results for two series of measurements made on two different samples are shown
in Figure 2. The general behavior of $\widetilde{D}_{Fe}$ decreasing with x as reported by Levin
and Wagner (and in subsequent measurements reported by Prof. Wagner at this
symposium) are confirmed but our diffusion coefficients are consistently lower
by about an order of magnitude. A possible explanation of this difference is
given below.

Discussion

Representative results presented in Table 1 illustrate clearly that the
Darken equation with $f \approx 1$ is not obeyed in this system. We feel that there
are two possible explanations for this result.

1. When the composition of FeO_x is suddenly changed near the surface there
is a change in lattice parameter. The shape of the sample will not be able to
change to accommodate this change in molar volume so that there will be a stress
gradient across the sample. To relieve this stress there will have to be a
flux of matter normal to the concentration gradient. If the stress gradient is
sufficiently large it is entirely possible that the rate of change of composition
is controlled by the rate of relaxation of stress, i.e. by diffusion of iron in
the absence of a concentration gradient (it is assumed that oxygen can be trans-
ported in the gas phase) as for example, in sintering.

In terms of the equations given above the chemical potential appearing in
eq. (3) must be replaced by[10]

$$\mu_{Fe} = \mu_{Fe}^O + RT \ln a_{Fe}^O + \delta\mu \tag{8}$$

where a_{Fe}^O is the activity of iron in the unstressed material and $\delta\mu$ is the
change in chemical potential due to the stress. Explicit expressions for $\delta\mu$

in terms of the stresses and elastic coefficients have been given by Darken, Li and Oriani.[10] Equation (6) becomes now

$$\tilde{D}_i = \frac{D_i}{f} \left[\frac{d\ln a_i}{d\ln c_i} + \frac{1}{RT} \frac{d(\delta\mu_i)}{d\ln c_i} \right] \tag{9}$$

Only the first term in square brackets is obtainable from equilibrium measurements. Evaluation of the second term requires a detailed knowledge of the elastic compliances of the crystal but it is important to note that it is of the opposite sign to the first term. We may illustrate this last point by a very rough approximation (not to be taken too seriously, but simply given to show that the effect of stresses must be taken into account) as follows. If the shear modulus is much greater than the bulk modulus we may suppose the stress to be essentially a hydrostatic pressure P given approximately by $P \approx -(1/\beta)(\Delta V/V)$ where β is the compressibility and $\Delta V/V$ the fractional change in volume of the material that would occur on changing the concentration. $\delta\mu$ is then $P\bar{V}_i \approx -(\bar{V}_i/\beta)(\Delta V/V)$ and finally

$$\frac{1}{RT} \frac{d(\delta\mu)}{d\ln c_i} \approx \frac{-\bar{V}_i}{\beta RT} \frac{d(\Delta V/V)}{d\ln c_i} \tag{10}$$

From the data of Jette and Foote[11] and Levin and Wagner[12] relating lattice parameter to composition we estimate $\bar{V}_{Fe} = 5.0$ cm^3 mole^{-1}, $d(\Delta V/V)/d\ln c_{Fe} = 0.4$, so that with $\beta \sim 10^{-6}$ atm^{-1} the right hand side of eq. (10) is equal to about -20 compared with about $+30$ for $d\ln a_{Fe}/d\ln c_{Fe}$.

This consideration is particularly important for a material of wide composition range such as wüstite. For an oxide like NiO$_x$ for example $d\ln a/d\ln c$ is of the order of 10^3 so that the second term in eq. (9) will be relatively unimportant.

2. We have still to explain the observation that $\tilde{D}_{Fe}$ decreases as x increases. This can be explained if f increases with increasing x, as is quite possible in a highly defective material such as wüstite.

In a system containing a dilute solution of vacancies jumping strictly at random f will be less than one due to the fact that tracer jumps are not random but sequentially correlated with a higher than statistical probability of an immediate return jump. If however one has a concentrated system of defects their jumps will no longer be random but on the contrary it is likely that there is correlation between two (or more) simultaneous atomic jumps. This will be because of interactions between defects such as vacancies making certain configurations more stable. Simultaneous jumps that preserve the integrity of the complex will then be preferred over random jumps.[*]

It is quite likely then that the decreasing $\tilde{D}$ observed in this system reflects an increase of f from 0.78 for a dilute solution of vacancies in the (hypothetical) material with x close to unity to a value somewhat greater than one in material with x ∼ 1.1. It is possibly significant in this connection that $\tilde{D}$ appears to level off at a composition close to the W1 → W2 transition of Raccah and Valiet[7] which is likely to represent an ordering of defect clusters.

Summary

Chemical diffusion in the FeO$_x$ (wüstite) system indicates that the Darken equation does not correctly predict the relationship between chemical and tracer

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[*]It is possibly helpful to consider tw. extreme examples. In a direct place exchange mechanism of diffusion by tracer atoms a net flux of matter (or ionic conductivity) is not possible so that f → ∞. By way of contrast the 'caterpillar' mechanism proposed by Yokota[13] and which consists essentially of simultaneous linear jumps. The net flux of atoms can be much greater than that of tracers so that f ≪ 1 (Note that f defined by Yokota is the reciprocal of that used in this paper).

diffusion coefficients. A modification of the Darken equation is proposed which takes into account the stresses present in an inhomogeneous material. The results also indicate that in very defective materials (such as wüstite) the correlation coefficient may well be concentration dependent.

Table 1

Observed and calculated[*] chemical diffusion coefficients in FeO_x

T°C	x	$10^6 \tilde{D}$ (calc)	$10^6 \tilde{D}$ (obs)	Author
1100	1.125-1.05	2.7	3.2	Levin and Wagner
1100	1.125 1.10	6.7	0.87	" " "
1055	1.07	2.5	0.15	This Work
1055	1.13	6.1	0.06	" "

[*] Calculated from eq. (6) with $f = 1$.

FeO$_{1.09}$

D_{Fe}^* (cm^2 sec^{-1})
$= (4.1 \cdot 10^{-3}) \exp(-27.8 \text{ kcal}/RT)$

• Carter & Richardson
○ Desmarescaux & Lacombe
× Himmel, Mehl & Birchenall
★ Pettit (oxidation)

Interdiffusion $O - FeO_x$ at 1055°C

Sample 2

Sample 3

$X = O/Fe$

$10^7 \times \tilde{D}$ (cm^2/sec)
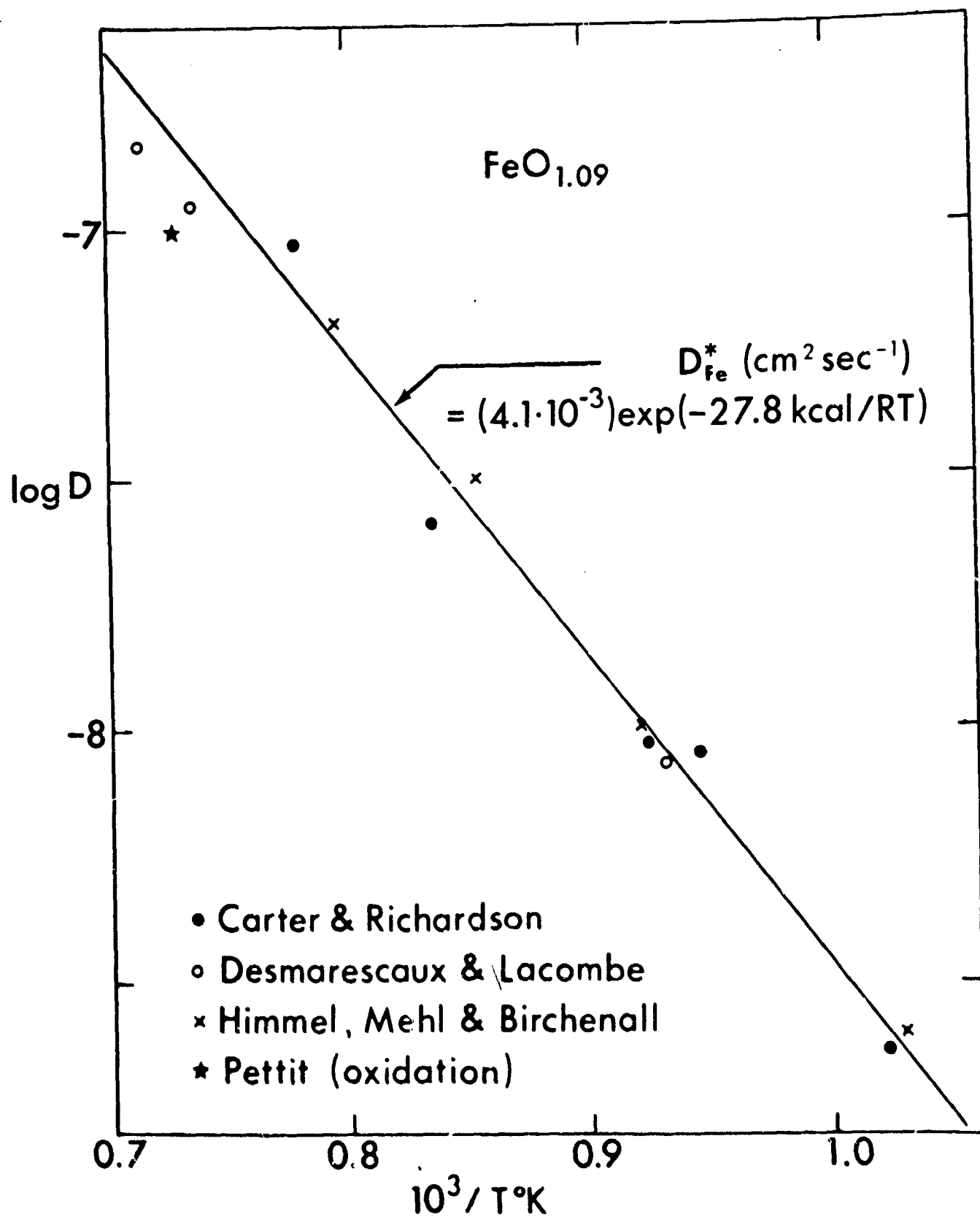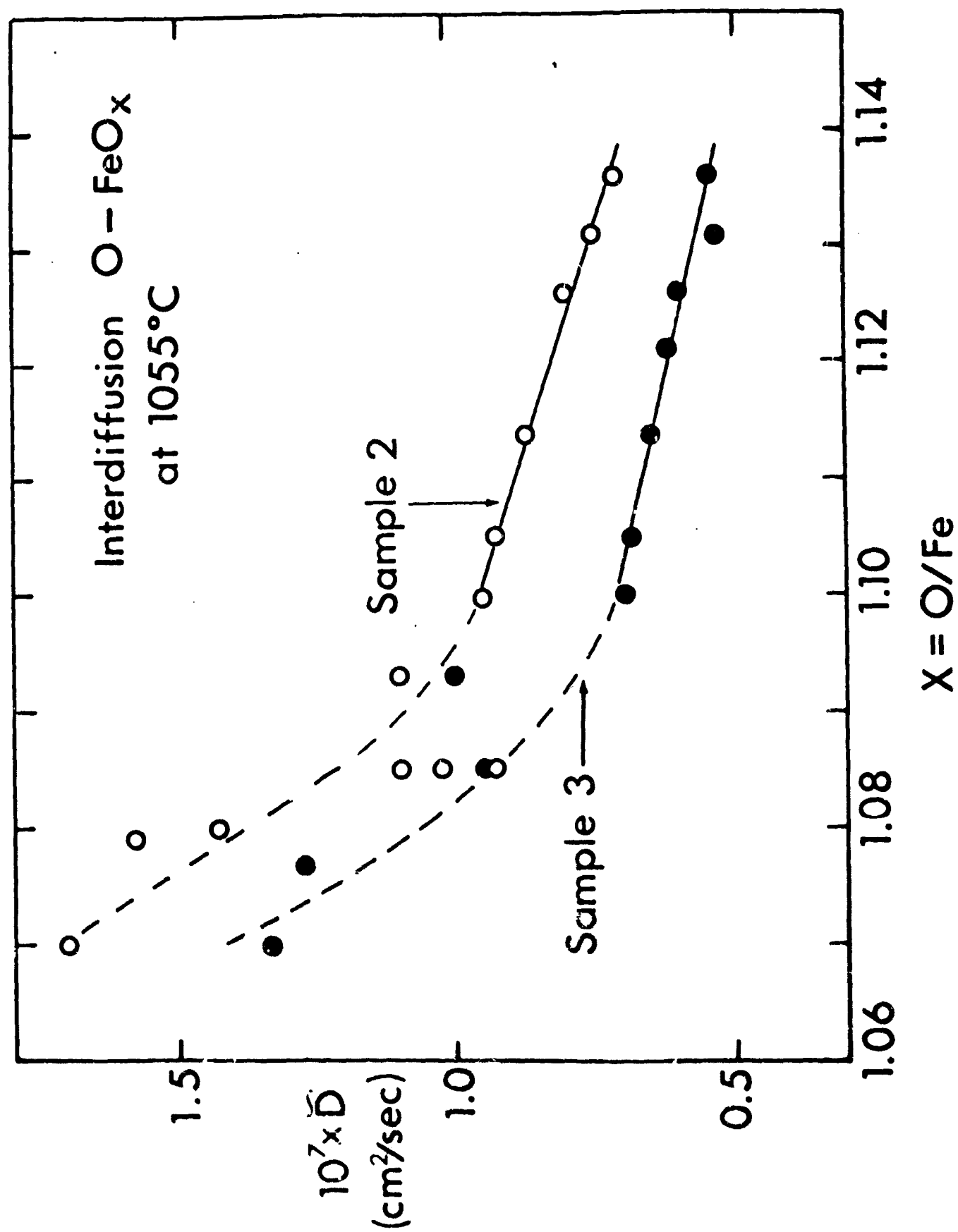
References

1. L. S. Darken, Trans. Met. Soc. AIME, 175, 184 (1948).

2. L. B. Pfeil, J. Iron and Steel Inst., 119, 501 (1929); 123, 237 (1931).

3. L. Kimmel, R. F. Mehl and C. E. Birchenall, Trans. Met. Soc. AIME, 197, 827 (1954).

4. R. E. Carter and F. D. Richardson, Trans. Met. Soc. AIME, 197, 1244 (1954).

5. P. Desmarescaux and P. Lacombe, Mem. Sci. Rev. Met., 60, 899 (1963).

6. L. S. Darken and R. W. Gurrey, J. Am. Chem. Soc., 67, 1398 (1945).

7. P. Raccah and P. Vallet, C. R. Acad. Sci. (Paris), 255, 1919 (1962).

8. B. Swaroop and J. B. Wagner, Trans. Met. Soc. AIME, 239, 1215 (1967).

9. R. L. Levin and J. B. Wagner, Trans. Met. Soc. AIME, 233, 159 (1965).

10. J. C. M. Li, R. A. Oriani and L. S. Darken, Z. phys. Chem. (N.F.), 49, 271 (1966).

11. E. R. Jette and F. Foote, J. Chem. Phys., 1, 29 (1933).

12. R. L. Levin and J. B. Wagner, Trans. Met. Soc. AIME, 236, 516 (1966).

13. I. Yokota, J. Phys. Soc. Japan, 21, 420 (1966).

Interdiffusion Coefficients from Conductivity Measurements

- Application to Cu_2O

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Introduction

In many non-stoichiometric oxides with ionized vacancies, the conductivity is proportional to the departure from the ideal composition. This is the case for example in CoO.[1] In Cu_2O the conductivity is accurately proportional to the square root of the vacancy concentration (as shown by the oxygen pressure dependence of conductivity[2] and vacancy concentration[3]). It would appear possible therefore to use conductivity as a measure of composition of the sample, and indeed several authors[4] have used this fact to follow the kinetics of interdiffusion in oxides.

It is necessary however to proceed with caution as in general the apparent conductance of an inhomogeneous sample is not proportional to the average concentration of defects. Provided that there is local electrical neutrality, (i.e. in the absence of a space charge) it is possible however, to relate the local conductivity σ to the local concentration of defects, c.

Theory

We have considered the case of a rectangular prism $-a_1 < x_1 < a_1$, $-a_2 < x_2 < a_2$, $-a_3 < x_3 < a_3$ with porous electrodes on the x_1, x_2 faces so that the conductance can be measured in the x_3 direction. We suppose that the initial conductivity σ_i is due to an initial homogeneous concentration of defects c_i. For times greater than zero the surface concentration is held at c_f so that the conductivity comes to a value σ_f as $t \to \infty$. The concentration at any point in the material is then given by the well-known expression

$$c\,(x_1,\,x_2,\,x_3) = c_f - (c_f - c_i)\,S\,(\xi_1)\,S\,(\xi_2)\,S\,(\xi_3) \tag{1}$$

where

$$S\,(\xi_1) = (2/\pi) \sum_{n=0}^{\infty} \left[(-1)^n/(n+1/2) \right] \exp\left[-\beta_1 (n+1/2)^2 \pi^2 \right] \cos\left[(n+1/2)\pi\xi_1 \right] \tag{2}$$

and in turn

$$\xi_i = x_i/a_i \quad ; \quad \beta_i = Dt/a_i^2 \tag{3}$$

The local conductivity is $\sigma(x_1, x_2, x_3)$ and as discussed above we have

$$\sigma(x_1, x_2, x_3) = A\left[c(x_1, x_2, x_3)\right]^m \tag{4}$$

with A a constant and m usually 1 or 1/2.

The apparent conductivity, $\bar{\sigma}$, measured in the x_3 direction is obtained by multiplying the conductance of the sample by the length/area ratio and is related to the local conductivity by

$$\bar{\sigma} = \frac{a_3}{2\,a_1 a_2} \left[\int_{-a_3}^{a_3} \frac{dx_3}{\int_{-a_1}^{a_1} \int_{-a_2}^{a_2} \sigma\, dx_2\, dx_1} \right]^{-1} \tag{5}$$

From eqs. (5), (4) and (1) one obtains after some manipulation

$$\sum = \frac{\sigma_f - \bar{\sigma}}{\sigma_f - \sigma_i} = \frac{1}{1-\alpha} \left[1 - \left(\int_0^1 I^{-1}\, d\xi_3 \right)^{-1} \right] \tag{6}$$

where $\quad I = \displaystyle\int_0^1 \int_0^1 \left[1 + (\alpha^{1/m} - 1)\, S\,(\xi_1)\, S\,(\xi_2)\, S\,(\xi_3) \right]^m d\xi_1\, d\xi_2$

and $\quad \alpha = \sigma_i/\sigma_f$

It is of interest to compare Σ as given by eq. (6) with the corresponding quantity $W \equiv (w_f - w)/(w_f - w_i)$ where w_f and w_i are the final and initial amounts of defects. The explicit expression for W is given in reference 4.

In Figure 1 we show W and Σ as a function of the dimensionless quantity Dt/a_3^2 for various shape samples and values of σ_f/σ_i for the case $m = 1$. It

may be seen that in general W and Σ are very close to each other for long, thin samples when σ_f/σ_i is not very different from unity. In other cases however the assumption that $\Sigma = W$ may lead to large errors in the calculated diffusion coefficients.

Application to Cuprous Oxide

Attempts to study interdiffusion in cuprous oxide using a vacuum micro-balance technique were severely limited by the nature of the material. Specifically, at temperatures above 1000°C evaporation is very rapid so that the small weight changes upon change of stoichiometry are hard to determine. At lower temperatures the cuprite phase field is very narrow, again precluding reliable measurements. For these reasons we decided to resort to electrical measurements in this system.

Two single crystal specimens were used; sample 1 was 4.50 x 4.65 x 6.34 mm and sample 2 was 1.91 x 1.91 x 15.9 mm. In each case the conductivity was measured along the longest direction using two probes. After equilibration at low oxygen pressure, oxygen was rapidly admitted to the sample and the conductivity monitored as a function of time. Strictly, in order to use the expressions derived above for Σ, porous contacts covering the whole face of the crystal should be used. The use of smaller contacts is likely to be less serious in the case of sample 2. As conductivity changes are very rapid, the sample current with known constant applied voltage was recorded with a recorder speed of 6 inches/minute. Plots of Σ versus log t were superimposed on theoretical plots of Σ versus log (Dt/a_3^2) calculated according to eq. (6). The difference in the abscissa of the two plots is equal to log (D/a_3^2) so that D is readily calculated. As the conductivity is very temperature sensitive it is quite possible to measure erroneous values of σ_f; however, this becomes evident when the experimental curve is compared to the theoretical curve, and any experimental

results differing significantly from the theory were rejected.

Because of the very rapid diffusion observed there was considerable scatter of the experimental results. These are reported in Table 1 with results for each crystal at each temperature reported as an average. The results for sample 2 were in general better and are in fair agreement with the theoretical values (discussed below). The results for sample 1 are too high; it is not clear at present whether this is due to the fact that the experimental conditions did not conform to the boundary conditions used in deriving eq. (6) or whether effects such as surface diffusion are significant.

Theory for Cuprous Oxide and Comparison with Experiment

We can calculate the expected interdiffusion coefficients as follows. Neglecting oxygen diffusion,[5] the rate of interdiffusion of oxygen and Cu_2O_{1+x} will be given by the Darken equation*

$$\widetilde{D} = D^*_{Cu} \; d\ln a/d\ln c \qquad (7)$$

where D^*_{Cu} is the tracer diffusion coefficient of copper in cuprous oxide. According to Moore and Selikson[6] at an oxygen pressure of 0.1 torr

$$\log_{10} D^*_{Cu} = -1.36 - 7900/T \qquad (8)$$

Under the same conditions it was found by O'Keeffe and Moore[3] by direct gravimetry that

$$\log_{10} x = 0.02 - 4760/T \qquad (9)$$

---

* Objections raised in the previous paper to the Darken equation are not valid here. This is because now $d\ln a/d\ln c$ is very large ($\sim 10^3$) and we are considering a dilute solution of vacancies ($< 0.1\%$).

with

$$\partial \ln x / \partial \ln P_{O_2} = 0.27 \tag{10}$$

Now setting $d\ln a/d\ln c = 1/2 \, d\ln P_{O_2}/d\ln (1+x)$ and recalling that $x \ll 1$ we obtain from eqs. (7) - (10)

$$\log_{10} \tilde{D} = -1.11 - 3140/T \tag{11}$$

Table 1 also records $\tilde{D}$ as calculated from eq. (11). The agreement with sample 2 is really quite remarkable when it is remembered that the three separate measurements being compared are all subject to large errors. Perhaps the most difficult measurement is that of the non-stoichiometry x and it is gratifying that the interdiffusion results do confirm the order of magnitude at least of the previously reported results.

The $\tilde{D}$ reported here may be interpreted as a vacancy diffusion coefficient. The very high diffusion coefficients are in accord with the observation that internal equilibrium can readily be reached in cuprous oxide down to very low temperatures.[2,7] It is worth remarking also that in general cation mobility is very high in the chalcogenides of the univalent metals.

Table 1

Measured and Calculated Values of $\log_{10} \tilde{D}$ in Cu_2O

T°C	Sample 1 [*]	Sample 2 [*]	Calculated [**]
933 ± 1	-3.4 (1)	-3.6 (2)	-3.71
973 ± 1	-3.15 (5)	-3.4 (2)	-3.63
1001 ± 1	.3.2 (3)	-3.75 (4)	-3.57
1032 ± 1	-2.6 (2)	-3.45 (3)	-3.51
1064 ± 1	-2.5 (2)	-3.4 (5)	-3.46

[*] Numbers in parentheses are the number of separate measurements at that temperature.

[**] Calculated from eq. (11).

Figure 1 - Theoretical curves for conductivity and weight change as a
function of time for various shape samples. The numbers on
the curves are the values of σ_i/σ_f. The curves labeled W
refers to weight change, the others to conductivity change.

Σ, W
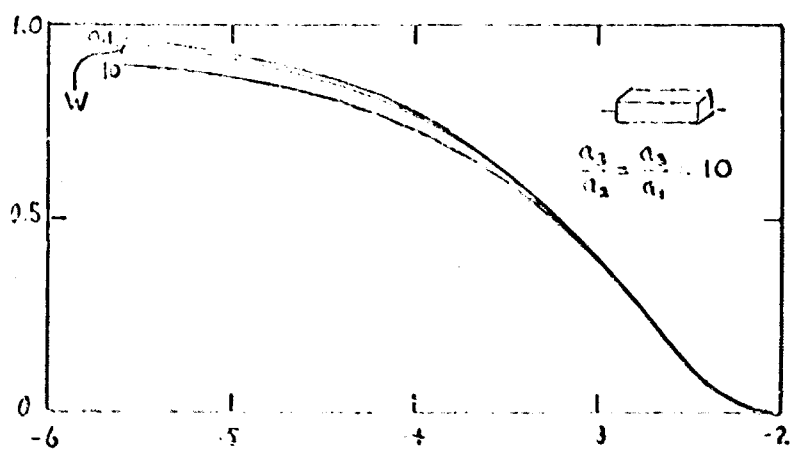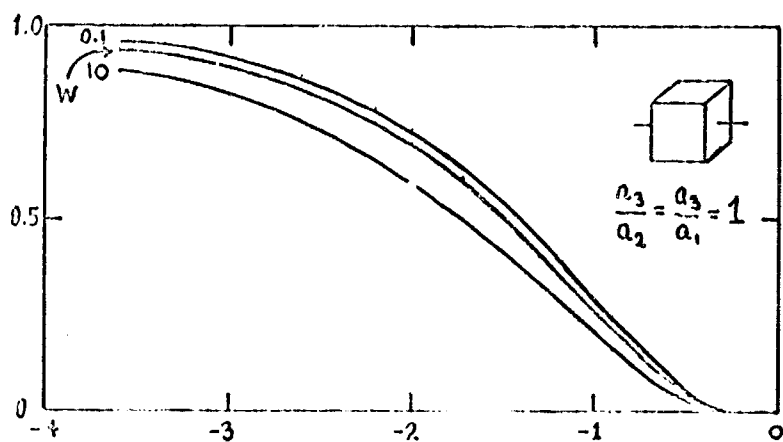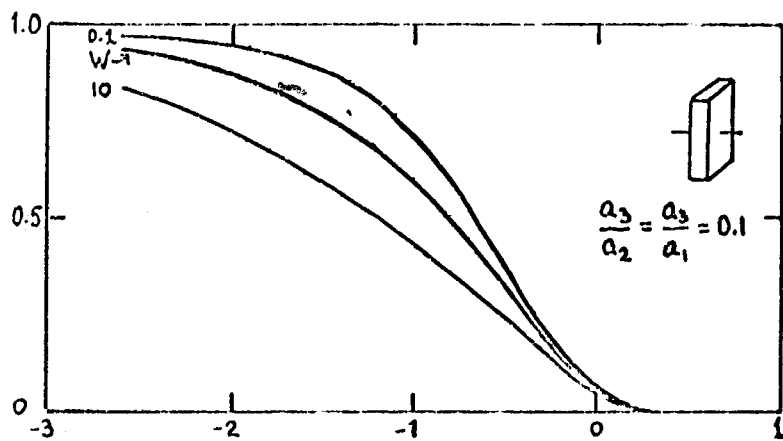
$\log(Dt/a_3^2)$

References

1. B. Fisher and D. S. Tannhauser, J. Electrochem. Soc., <u>111</u>, 1194 (1964).

2. R. S. Toth, R. Kilkson and D. Trivich, Phys. Rev., <u>122</u>, 482 (1961); . .

   M. O'Keeffe and W. J. Moore, J. Chem. Phys., <u>35</u>, 1324 (1961).

3. M. O'Keeffe and W. J. Moore, J. Chem. Phys., <u>36</u>, 3009 (1962).

4. J. B. Price and J. B. Wagner, Z. phys. Chem. (N.F.), <u>49</u>, 257 (1966);

   L. C. Walters and R. E. Grace, J. Phys. Chem. Solids, <u>28</u>, 245 (1967);

   D. G. Thomas, J. Phys. Chem. Solids, <u>3</u>, 229 (1957).

5. W. J. Moore, Y. Ebisuzaki and J. Sluss, J. Phys. Chem., <u>62</u>, 1438 (1958);

   M. O'Keeffe, Y. Ebisuzaki and W. J. Moore, J. Phys. Soc. Japan, <u>18</u>, 131 (1963).

6. W. J. Moore and B. Selikson, J. Chem. Phys., <u>19</u>, 1539 (1951); <u>20</u>, 927 (1952).

7. M. O'Keeffe and F. S. Stone, Proc. Roy. Soc. (Lond.), <u>A267</u>, 501 (1962).

A Fortran Program to calculate conductivity and weight as a function of time during interdiffusion.*

The following program is designed to calculate Σ and W as described in the previous paper. The necessary input data are provided on three cards.

card (a)   title in alphanumeric form in columns 1-80

card (b)   m as a floating point number in columns 1-10

card (c)   the values of a_3/a_1, a_3/a_2 and σ_i/σ_f in columns 1-10, 11-20,
21-30. For the most useful range of output a_2 should be $\geq a_1$.

This set of three cards may be repeated for each sample; the final card after all the sets should be blank.

The output is   BETA3 $\equiv \beta_3 \equiv Dt/a_3^2$, $\log_{10}(\beta_3)$, Σ and W.   In the heading LZ/LX $= a_3/a_1$; LZ/LY $= a_3/a_2$.

The program has been found to run well for m $=$ 0.5 and 1 (in the latter case a much simpler program could be devised) and for $\sigma_i/\sigma_f < 1$. The program is doubtless inefficient but the demand in computer time is modest so that little effort has been made to streamline it. A series of calculations for one sample takes about five minutes using a CDC 3400 computer.

---

* written by W. J. Kass.

C

C

P302

```
                  PROGRAM DIFCON
C     PROGRAM TO DETERMINE DIFFUSION COEFFICIENTS FROM CONDUCTIVITY
C     MEASUREMENTS
C     BRUTE FORCE INTEGRATION
C     OMEGA MUST BE LESS THAN 1  (GAS UPTAKE)
C     OMEGA = SIGMA INITIAL / SIGMA.FINAL
C     EM    = DEPENDENCE OF SIGMA ON CONCENTRATION, THAT IS,
C             SIGMA = CONSTANT*CONCENTRATION**EM
C     A32   = A3/A2  LENGTH OF Z AXIS OF CRYSTAL / LENGTH OF LONGEST O
C             X OR Y AXES
C     A31   = A3/A1 LENGTH OF Z AXIS OF CRYSTAL / LENGTH OF SHORTEST O
C             X OR Y AXES
C     A31 SHOULD BE A LARGER NUMBER THAN A32
      COMMON SK(50), PROD(50), A31, A32, BETA3, XI3, OMEGA, EM
      DIMENSION TITLE(20)
      LOG10F(X) = LOGF(X)/2.3025851
      PI = 3.1415926536
  944 READ 970, (TITLE(I), I = 1, 20)
  970 FORMAT(20A4)
      READ 900, EM
   42 FORMAT(1H1)
      IF(EM) 943, 942, 943
  943 READ 900, A31, A32, OMEGA
  900 FORMAT(3F10.0)
      PRINT 972
  972 FORMAT(1H1)
      PRINT 970,(TITLE(I), I = 1, 20)
      PRINT 910, EM, OMEGA
  910 FORMAT(    5H  M =, F6.3,10X, 19HSIGMA I / SIGMA F =, F7.4)
      PRINT 911, A31, A32
  911 FORMAT(9H  LZ/LX =, F8.4, 4X, 7HLZ/LY =, F8.4 //)
      PRINT 926
  926 FORMAT(6X, 5HBETA3, 5X, 9HLOG(BETA), 5X, 5HSIGMA, 6X, 6HWEIGHT)
      A = 10.0*LOG10F(A31)
      KLOG = A
      AA = KLOG
      AALOG = AA/10.0
      BETLOG = -4.5 - 2.0*AALOG
  909 DO 950 NIN = 1, 50
      BETLOG = BETLOG + 0.1
      BETA3 = EXPF(BETLOG*2.3025851)
      PROD(1) = 0.0
      CALL SIMPSON(SIMP)
      SIGMA = (1.0/(1.0 - OMEGA))*(1.0 - (1.0/SIMP))
      BETA1 = A31*A31*BETA3
      BETA2 = A32*A32*BETA3
      CALL SIMPWT(BETA1, WTX, EM)
      IF(A31 - A32) 960, 961, 960
  961 WTY = WTX
      GO TO 967
  960 CALL SIMPWT(BETA2, WTY, EM)
  967 IF(A31 - 1.0) 962, 963, 962
  963 WTZ = WTX
      GO TO 965
  962 IF(A32 - 1.0) 964, 966, 964
  966 WTZ = WTY
```

```
            GO TO 965
        964 CALL SIMPWT(BETA3, WTZ, EM)
        965 WTCHNG = WTX*WTY*WTZ
            PRINT 925, BETA3, BETLOG, SIGMA, WTCHNG
        925 FORMAT(F13.6, F11.4, F12.4, F11.4)
            IF(SIGMA - 0.0001) 944, 930, 930
        930 CONTINUE
            GO TO 944
        942 CALL EXIT
            END
```

```
            SUBROUTINE SIMPSON(SIMP)
            COMMON SK(50), PROD(50), A31, A32, BETA3, XI3, OMEGA, EM
            NINCZ = 40
            ZINC = 0.025
            XI3 = 0.0
            CALL BINOM(BINT)
            SIMP = ZINC/(3.0*BINT)
            BINT1 = 1.0/BINT
      C     PRINT 41, BETA3,XI3, BINT1, SIMP
            DO 30 JSIMP = 1, NINCZ
            AJSIMP = JSIMP
            XI3 = ZINC*AJSIMP
            IF(JSIMP - NINCZ) 26, 27, 27
         26 IF(XMODF(JSIMP, 2)) 28, 29, 28
         28 CALL BINOM(BINT)
            PANEL = 4.0*ZINC/(BINT*3.0)
            SIMP = SIMP + PANEL
            BINT1 = 1.0/BINT
      C     PRINT 41, BETA3,XI3, BINT1, SIMP
            GO TO 30
         29 CALL BINOM(BINT)
            PANEL = 2.0*ZINC/(BINT*3.0)
            SIMP = SIMP + PANEL
            BINT1 = 1.0/BINT
      C     PRINT 41, BETA3,XI3, BINT1, SIMP
            GO TO 30
         27 CALL BINOM(BINT)
            PANEL =      ZINC/(BINT*3.0)
            SIMP = SIMP + PANEL
            BINT1 = 1.0/BINT
      C     PRINT 41, BETA3,XI3, BINT1, SIMP
         30 CONTINUE
         41 FORMAT(7H BETA3=, F10.5, 5X 5HXI3 =, F7.4, 5X 10H1./BINT =,
           1 E12.5, 5X 6HSIMP =, E12.5)
            RETURN
            END
```

```
                    SUBROUTINE SXI(BETA, XI, S)
      C      COMPUTATION OF SERIES FOR S   TO BE USED IN SIMPSON INTEGRATION
      C      TO OBTAIN INTEGRAL OF S**K
             IF(BETA - 0.0003) 112, 112, 113
      112  IF(XI - 0.9)          114, 114, 115
      113  IF(BETA - 0.001 ) 117, 117, 118
      117  IF(XI - 0.8)          114, 114, 115
      118  IF(BETA - 0.003 ) 122, 122, 123
      122  IF(XI - 0.7)          114, 114, 115
      123  IF(BETA - 0.01  ) 127, 127, 128
      127  IF(XI - 0.4)          114, 114, 115
      128  IF(BETA - 0.03  ) 132, 132, 115
      132  IF(XI - 0.0)          114, 114, 115
      114  S = 1.0
             RETURN
      115  CONTINUE
             PI = 3.1415926536
             S = 0.0
             DO 310 MM = 1, 100
             NPT = MM - 1
             ANPT = NPT
             ANPH = ANPT + 0.5
             ARG = BETA*ANPH*ANPH*PI*PI
             IF(ARG - 175.0) 308, 308, 309
      308  FAC1 = 1.0/EXPF(ARG)
             GO TO 306
      309  TERM = 0.0
             GO TO 331
      306  FAC2 = COSF(ANPH*PI*XI)
             IF(XMODF(NPT,2)) 304, 305, 304
      305  FAC3 = 2.0/(ANPH*PI)
             GO TO 302
      304  FAC3 = -2.0/(ANPH*PI)
      302  TERM = FAC3*FAC1*FAC2
             IF(ABSF(FAC2  ) - 1.0E-05) 303, 303, 327
      327  IF(NPT - 3) 303, 303, 328
      328  IF(ABSF(TERM/S ) - 1.0E-05) 331, 331, 303
      303  S = S + TERM
      310  CONTINUE
             RETURN
      331  S = S + TERM
      340  FORMAT(6H NPT =, I3, 10X, 3HS =, F9.5, 10X 6HTERM =, E12.5)
             RETURN
             END
```

```
        SUBROUTINE PRODSK
C       SUBROUTINE TO  DETERMINE PRODUCT OF SK(BETA1)*SK(BETA2)
        COMMON SK(50), PROD(50), A31, A32, BETA3, XI3, OMEGA, EM
        IF(PROD(1)) 710, 711, 710
    710 RETURN
    711 BETA = BETA3*A31*A31
C       IF(A31 - A32) 750, 751, 750
C 750 PRINT 735, BETA3, BETA
    735 FORMAT(9H BETA 3 =, F10.6, 10X, 8HBETA 1 =, F10.6)
C       GO TO 782
C 751 PRINT 733, BETA3, BETA
    733 FORMAT(9H BETA 3 =, F10.6, 10X, 17HBETA 1 = BETA 2 =, F10.6)
C 782 PRINT 172
    172 FORMAT(6H   XI , 5X, 5HS    , 3X, 3HC  , 40X, 5HSK(K))
        CALL SIMP12(BETA)
        DO 720 MN = 1,25
    720 PROD(MN) = SK(MN)
        IF(A31 - A32) 716, 717, 716
    716 BETA = BETA3*A32*A32
C       PRINT 734, BETA3, BETA
    734 FORMAT(9H BETA 3 =, F10.6, 10X, 8HBETA 2 =, F10.6)
C       PRINT 172
        CALL SIMP12(BETA)
        DO 730 MN = 1,25
    730 PROD(MN) = PROD(MN)*SK(MN)
        RETURN
    717 DO 740 MN = 1,25
    740 PROD(MN) = SK(MN)*SK(MN)
        RETURN
        END
```

```
        SUBROUTINE BINOM(BINT)
        COMMON SK(50), PROD(50), A31, A32, BETA3, XI3, OMEGA, EM
        BINT = 1.0
        BCOEF = 1.0
        DO 830 KBI = 1, 25
        K = KBI
        AKBI = KBI
        BCOEF = BCOEF*(EM-AKBI+1.0)/AKBI
        FAC1 = (OMEGA**(1.0/EM) - 1.0)**K
        CALL SXI(BETA3, XI3, S)
        FAC2 = S**K
        CALL PRODSK
        FAC3 = PROD(KBI)
        TERM = BCOEF*FAC1*FAC2*FAC3
        IF(KBI - 1) 832, 832, 828
    828 IF(ABSF(TERM/BINT) - 1.0E-05) 831, 831, 832
    832 BINT = BINT + TERM
    830 CONTINUE
        RETURN
    831 BINT = BINT + TERM
    840 FORMAT(4H K =, I3, 10X, 6HBINT =, F12.5, 10X, 6HTERM =, F12.5)
        RETURN
        END
```

```
      SUBROUTINE SIMP12(BETA)
C     SUBROUTINE FOR SIMPSON INTEGRATION OF S(XI1), S(XI2) TO GIVE ALL
      COMMON SK(50), PROD(50), A31, A32, BETA3, XI3, OMEGA, EM
      PI = 3.1415926536
      XI = 0.0
      ZINC = 0.020
      NINCZ = 50
  111 CALL SXI(BETA, XI, S)
  150 DO 152 MN = 1, 25
  152 SK(MN) = ZINC*S**MN/3.0
      C = 1.0
C     PRINT 171, XI, S, C, (SK(L), L = 1,9)
      DO 180 JSIMP = 1, 49
      AJSIMP = JSIMP
      XI = AJSIMP*ZINC
  115 CALL SXI(BETA, XI, S)
  139 IF(XMODF(JSIMP,2)) 140, 141, 140
  140 DO 142 MN = 1, 25
      PANEL = 4.0*ZINC*S**MN/3.0
  142 SK(MN) = SK(MN) + PANEL
      C = 4.0
C     PRINT 171, XI, S, C, (SK(L), L = 1,9)
      GO TO 180
  141 DO 144 MN = 1, 25
      PANEL = 2.0*ZINC*S**MN/3.0
  144 SK(MN) = SK(MN) + PANEL
      C = 2.0
C     PRINT 171, XI, S, C, (SK(L), L = 1,9).
  171 FORMAT(F6.3, F10.5, F6.1, 9F10.5)
  180 CONTINUE
C     PRINT 172, (SK(L), L = 1, 9)
  172 FORMAT(22H 1.000   0.00000    1.0, 9F10.5)
C     PRINT 173
  173 FORMAT(1H1)
      RETURN
      END
```

```
      SUBROUTINE SIMPWT(BETA,WT,EM)
C     COMPUTATION OF CONDUCTIVITY CHANGE AS CALCULATED BY WEIGHT
C     CHANGE FORMULAS
      PI = 3.1415926536
      SUM = 0.0
      DO 480 K = 1, 100
      AN = K - 1
      TERM = (1.0/(AN+0.5)**2)*EXPF(-BETA*PI*PI*(AN + 0.5)**2)
      IF(TERM - 1.0E-06) 481, 481, 480
  480 SUM = SUM + TERM
  481 WT = (2.0/(PI*PI))*(SUM + TERM)
      RETURN
      END
```

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13. ABSTRACT

This report summarizes the research on semiconducting properties of cuprous oxide performed under grant AS-AFOSR-719-65. Contributions have been made to the understanding of the behavior of cuprous oxide at high temperatures with special reference to the electrical properties and defect structure. Interdiffusion studies by thermogravimetric means have been made on wüstite and manganous oxide. Further work is being continued under grant AF-AFOSR-68-1371.

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